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THE CHEMISTRY
OF
IRON AND STEEL MAKING

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THE CHEMISTRY
OF
IRON & STEEL MAKING

AND OF THEIR PRACTICAL USES

BY

W. MATTIEU WILLIAMS, F.C.S., F.R.A.S.

FORMERLY CHEMIST IN THE WORKS OF SIR JOHN BROWN AND CO. LTD.

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PREFACE

THIS Treatise fulfils a promise made about twenty years ago to an audience of intelligent men, who listened very attentively to a few Lectures I delivered to them on the Chemistry of their Daily Work. They were employed in the iron and steel works of Sir John Brown & Co., Sheffield, where I was also employed as chemist to the works.

The first step towards such fulfilment was made in some 'Papers on Iron and Steel,' contributed to 'Nature' in 1870 and 1871; the second, by 'The Cantor Lectures on Iron and Steel,' delivered before the Society of Arts in 1876, and published by the Society; the third, and most complete, by a series of articles on 'The Rationale of Practical Metallurgy,' commenced in 'Iron,' April 1882, and continued during that and the following two years. These form the basis, though by no means the whole, of the present work.

I found that the four or five thousand men employed in the great works above-named might be divided into three classes: the first (and, I am sorry to say, the largest) neither knew, thought, nor cared anything about the scientific basis of their work; the second class treated 'the

doctor's shop'—as they called my laboratory—with contempt, and resented my interference with their work. The third class had, for the most part, passed through both these first and second stages of technological evolution, and were awakening to a perception of the fact that practical men like themselves might, after all, learn something from the 'theorists'—a name they had recently learned to apply to all who made any pretensions to scientific attainments.

The men who had reached this stage rapidly developed a desire for more and more scientific knowledge, each additional step increasing the desire for further progress—'as if increasing appetite had grown by what it fed on'; but in their efforts to make such progress they suffered much discouragement from the lack of any means of obtaining *direct* instruction in what they directly required.

What they wanted to learn, and still are craving to learn, is the why and the wherefore of the operations they are daily performing, and the nature and mode of action of the forces which effect the changes they daily witness. This is not *technical* education, but *technological* education; not the teaching by outsiders of the *technos*, or trade, which the workman has already learned in his shop, but the teaching of the *logos*, of the rationale, of that *technos*, or trade.

Neither do these men require elaborate treatises on hypothetical atom-piling and molecule-splitting, nor a re-hash of mere scholastic treatises, nor lecture-repetitions of the courses of instruction that have been received in the curriculum of university graduates; nor any other scholastic or book-makers' routine, having no direct con-

nection with their work. The forcing of these upon them has a serious tendency to drive them back again into the second class.

Having learned what they really do want, I have endeavoured to supply the required information in the simplest language consistent with scientific accuracy, explaining, as I proceed, the scientific terms that must be used, and that are not likely to be already understood.

As its title indicates, this work is limited to the chemical technology of the subject, for the simple reason that it is the branch that I have specially studied, both in theory and practice; the other element—viz., the engineering technology—can only be treated satisfactorily by one who is similarly qualified as a scientific engineering specialist.

I venture to hope that not only those who are directly employed in iron and steel making and working may find this treatise instructive: but that it will be readable and interesting to all intelligent Englishmen—or rather Britons—who desire to learn something concerning the mysteries of the most remarkable, the most successful, and the most exclusively national of all our British industries—the one which, as explained in the body of the book, owes its marvellous modern progress to British invention, British enterprise, and British industry; which is simply a product of British brain and muscle, scarcely a step of any importance having been made outside of the British Islands.

I further venture to hope that scientific chemists (who may skip the second chapter) will find something worthy of their attention in my struggles to explain some of the

chemical mysteries of the Blast Furnace, of the Puddling Furnace, and Mill Forge, besides those of the Cementing Chamber, the Bessemer Converter, and the protean constitution of steel.

In some cases I have been compelled to differ from high scientific authorities; but wherever this occurs I have carefully stated the conclusions as my own, and have described the experiments or other data upon which they are founded, in order that the reader may take them for what they are worth, and accept or reject them accordingly. This has enforced a certain amount of egotism, which I hope the reader will not misunderstand.

W. M. W.

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THE CHEMISTRY
OF
IRON AND STEEL MAKING

CHAPTER I

INTRODUCTORY

A NAKED MAN, unaided by weapons, tools, and other appliances, is about the most feeble of all the animals. He has neither teeth, nor claws, nor horns, nor hoofs, with which he can defend himself against other animals of his own size, nor sufficient speed of foot or climbing power to escape them. The duration of his utterly helpless infancy is longer than that of any other living creature; and yet he has become the master of all.

This mastery is due to the fact that he has supplemented his original feebleness by constructing weapons, tools, and implements, and using them intelligently.

The rudest savages that have yet been found have weapons and tools of some kind. The 'black fellows' of Australia—about the lowest of all, and living in a country which originally produced no rival more formidable than a kangaroo—invented the boomerang and other rude weapons. The Papuans of New Guinea, though without

metals when first discovered, made spear-heads of flint, and other weapons and tools of similar material.

Those who have studied the pre-historic vestiges of humanity—the remains of ancient man found in caverns and bedded in rock—divide the earliest annals of the race into three great periods or ages: the Stone, the Bronze, and the Iron periods. The Stone period is distinguished by the absence of any trace of metal among human remains and the abundance of flint implements, with a few stone vessels, showing how the rudest of our primitive ancestors supplemented the functions of their teeth and finger-nails by using the hardest and handiest things that could be picked up on the *surface* of the earth.

The earliest of these flint implements are rudely chipped, and left in the rough. They have been named '*paleolithic*' (ancient stone). After a long time there came some refinement and artistic feeling among these savages. They then smoothed and polished very laboriously their stone spear-heads, arrow-tips, hatchets, &c., with some regard to elegance of form. These are called '*neolithic*' (newer stone); but still there were no metals yet discovered and used, though the length of the *paleolithic* and *neolithic* periods must have been enormous.

Then a great stride was made, as we learn by exhuming human remains associated with weapons and implements of bronze, with here and there some ornaments of gold. The magnitude of this stride is evident when we reflect on the fact that the production of bronze implements demands a knowledge of the arts of reducing metallic ores, alloying, casting, forging, and working the metals. Besides this, the ancient bronze is susceptible of a certain degree of hardening and tempering, and it appears that the artificers of the Bronze period understood

and applied this property, which enabled them to make tools of bronze capable of fashioning the same metal in its soft state.

In the absence of direct and sufficient historical evidence, I will venture to supplement our dim knowledge of these distant epochs by some metallurgical inferences which afford fair ground for concluding that the wide gap of human progress between the Flint and Bronze periods was bridged over by a Gold period—that gold was the first metal discovered and used by man.

The grounds upon which I base this conclusion are the following:—

Gold is found *in its metallic state*, and nearly pure, *upon the surface of the earth*. Although existing in such small quantities in any given place, it is one of the most widely diffused of the heavy metals. The beautiful colour and lustre of a nugget or grain of gold would attract the attention of the neolithic savage; and the facility with which it may be beaten into shape by stone tools would afford him his earliest ideas of a metal and its properties. Silver also exists in the metallic state, but is rarely, if ever, found on the surface.

Excepting platinum and its rare companions, the metal which, next to silver, is the most liable to occur in the solid and metallic state, is copper. Men who had already learned to value gold would not pass unheeded an accidental discovery of a vein of native copper, and would probably struggle to utilise its most common ore—the gold-like, copper pyrites—which is so easily reduced, that an attempt to fuse it in a wood fire would effect the separation of more or less perfect metal; while the same attempt made upon the similarly gold-like, iron pyrites would certainly fail.

But why should the other constituent of bronze—the tin—have preceded iron, seeing that it does not occur in the metallic state, and that its ore is an oxide having no metallic lustre, but of stony or earthy aspect? To this fair question I will venture to supply an hypothetical answer:—

Before metallic cooking-vessels were constructed, water was boiled in vessels of rudely-baked clay, by throwing heated pebbles into it. The Cornish savages who performed this operation on the banks of the streams where they were the most numerously settled, inevitably picked up tin-stones with the other pebbles; these, when heated in a wood fire, must have become deoxidised and fused, and thus buttons of a bright, silvery, malleable metal would be found among the ashes of the spent fire.

As copper pyrites exist side by side with the tin-stone of Cornwall, it is not improbable that an accidental alloy of copper and tin may have been made there, at a very early date, by the reduction and fusing of both in the same fire.

These, I think, are good metallurgical reasons for the early appearance of England on the field of history; they explain why, during the Age of Bronze, its south-west shores should have been visited by those most ancient of ancient mariners, the Phœnician merchants, and why it was called by them the 'Land of Tin.' It is a very remarkable feature of our national history, that our metallurgical supremacy should have commenced so early, and have been so long and consistently maintained in both the Bronze and the Iron periods.

The much greater difficulty of obtaining iron from its ores, in spite of their great abundance, accounts for the long-continuance of the Bronze period, and indicates

the progress that was made in passing from the Bronze to the Iron age of human evolution. Pure iron is practically infusible without oxidation, excepting in furnaces of very special construction; and even its more fusible compounds, such as steel and cast-iron, demand a blast.

I have little doubt that the production of steel preceded that of iron. The ore that would first be used is that which presents the most metallic appearance, and is the most easily reduced—viz., magnetic oxide. It occurs superficially, is nearly pure, and contains more than 72 per cent. of iron. This, if reduced in a small furnace, with charcoal fuel and a moderate blast, would produce mild steel rather than iron. The samples of ancient iron, so-called, are all, as far as I can learn, composed of iron with ¼ per cent. and upwards of carbon.

Historical records tell us more of ancient steel than of ancient iron, and the native Hindoo and Burmese ironmakers of the present day, as well as those of Borneo, Africa, Madagascar, &c., all produce fine steel directly from the ore, and more easily and cheaply than they can make malleable iron.

The primitive ironmakers were but little troubled with the sulphur and phosphorus that afford so much exercise for the ingenuity of modern ironmakers. The reason of this early exemption from the troubles connected with the above-named impurities is that the purest and richest ores, and the purest of fuel, were the first to be used. The phosphorus that worries our modern ironmaster is derived from the inferior ores, which he uses on account of their great abundance. The same is the case with the silicon impurity. The sulphur is chiefly added by his fuel. He uses coal instead of wood for the same reason that he uses the inferior ores—

viz., because his demand for quantity exceeds the supply of the purer materials.

The primitive ironmaster, who made pounds where we now produce tons, could use the best; in fact, he was unable to use anything else, for reasons that are evident enough when we compare his simple method with those now in use. Besides this, he was not likely to recognise the poorer ironstones as containing any metallic elements at all. They are earthy in appearance, while the ores that we know he used have some degree of metallic lustre, and are more weighty in proportion to their bulk.

I must resist the temptation to describe the methods and apparatus of the early makers of charcoal-iron, and steel—it would carry me too far away from the more practical business of this treatise. Those who desire to study the archæology of iron-making will find much information in Dr. Percy's *Metallurgy*, vol. i.

I therefore pass at once to the next great step, which constituted the culmination of the Iron age of human progress—viz., the reduction of iron ores by means of coal, or fossil fuel—a step as peculiarly English as the supply of tin to the ancient world through the Phœnician merchants.

This was first practically achieved by a very remarkable and most unfortunate man, a martyr too little known to his fellow-countrymen. The ironmasters of Britain have not yet honoured themselves by erecting any kind of monument in honour of DUD DUDLEY.

The story of his struggles is recounted by himself in a quaint and curious volume, entitled, 'Dud Dudley's *Metallum Martis*: or IRON made with Pit-coale, Sea-coale, &c. And with the same Fuell to Melt and Fine Imperfect

Mettals and Refine Perfect Mettals. LONDON: Printed by T. M. for the Author. 1665.'

In the following abstract I have followed the *Metallum Martis* pretty closely, eliminating its abundant repetitions:—

The patent for Dudley's invention was granted to his father, Edward, Lord Dudley, February 21, 1621, for 'The misterie and arte of melting iron ewre, and of making the same into cast workes or barrs with sea-coles or pit-coles in furnaces with bellowes.'

This was preceded by other attempts in the same direction, which are thus described by Dud Dudley himself:—King James 'did in the 9th year of his reign grant his Letters Pattents of Privilege unto *Simon Sturtevant*, Esq., for 31 years, for the making of iron with pit-cole and sea-cole for the preservation of wood and timber of Great Brittain, so greatly then consumed in ironworks. This invention was by King James's command to be put in print, which book did contain near a quire of paper in quarto, called *Simon Sturtevant*, his *Metallica*. Anno 1612, May 22. Printed by *George Eld, cum Privilegio.*'

'After *Simon Sturtevant* could not perform his making of iron with pit-cole or sea-cole, according to his engagement, King *Iames* and Prince *Henry* caused him to render up his pattent, and a new pattent was granted unto *Iohn Rovenson*, Esq., who was also enjoyned to write a book of his inventions called *Rovenson's Metallica*, Printed for *Thomas Thorp, cum Privilegio;* May 15th, An. 1613.'

'After *Iohn Rovenson*, Esq., had often failed with his inventions and great undertakings — *Gumbelton*, Esq., a servant of Queen *Ann's*, undertook (by pattent) to perform the invention of making iron with pit-cole and sea-cole; but he, being as confident as others, did erect his works at *Lambeth*, which the author viewed; and *Gumbelton* failing,

the learned and ingenious Doctor *Jorden*, of *Baths*, the author's acquaintance, and sundry others, obtained pattents for making of iron and melting of mines with pit-cole and sea-cole, for the preservation of wood and timber; all which inventions and endeavours to effect and perfect the said works, have been by many hitherto well known to have worthily attempted the said invention, though with fruitless success.'

Dudley proceeds to state how he had seen and apparently studied these failures, and held it his duty 'to endeavour, if it were possible, to effect and perfect so laudable and beneficial, and, also, so much-desired inventions'; and how, 'having former knowledge and delight in the ironworks of my father's when I was but a youth; afterward, at 20 years old, was I fetched from *Oxford*, then of *Baliol College*, *Anno* 1619, to look and manage 3 ironworks of my father's, 1 furnace, and 2 forges, in the Chase of *Pensnet*, in *Worcestershire*; but wood and charcole growing then scant, and pit-coles, in great quantities, abounding near the furnace, did induce me to alter my furnace, and to attempt, by my new invention, the making of iron with pit-cole.'

He then states that he was sufficiently 'animated' by the result of his first trial to make 'a second blast and tryal,' and found the quality of iron to be good and profitable, but the quantity did not exceed three tons per week.

After this, his father, Lord Dudley, obtained the patent above referred to, the details of which are rather artfully concealed in the '*Metallum Martis*.' As the specification, like others of the time, was not enrolled, we can obtain no other information concerning it than is suggested by occasional allusions in the course of Dudley's rather rambling plaint and dissertation.

About a year after the grant of the patent, Dudley sent to the Tower 'much good merchantable iron,' which by King James's command was 'tryed by all Artists, and they did well approve of the iron.' His works were 'a furnace or ironwork in the Chase of *Pensnet* in the County of *Worcester*, besides cast-iron works of sundry sorts with pit-coles; and also, at two forges or iron mills, called *Cradley Forges*, fined the said iron into merchantable good bar iron.'

Just at this time came a great flood, known as the 'May-day Flood,' which 'not onely ruinated the authour's ironworks, but also other men's ironworks.' Dudley repaired his works, and was about to recommence, when the 'ironmasters whose works scaped the flood, and had often disparaged the authour's inventions, because the authour sold good iron cheaper than they could afford it,' complained to King James that Dudley's iron 'was not merchantable,' a complaint which was sufficiently refuted by their own persevering animosity. Had it not been merchantable, it could not have affected them.

The representations of the ironmasters 'so far prevailed with King James' that Dudley was commanded, 'with all speed possible, to send all sorts of bar iron up to the Tower of *London*, fit for making of musquets, carbines, and iron for great bolts, fit for shipping, which iron being so tryed by artists and smiths, that the ironmasters and ironmongers were all silenced.'

Only a few months after this the Parliament abolished monopolies, 'and diverse of the ironmasters endeavouring to bring the invention of making iron with pit-cole, sea-cole, peat and turff within the compasses of a monopoly; but the Lord Dudley and the authour did prevaile, yet the pattent was limited to continue but fourteen years. Then

Dudley 'went on with his invention cheerfully, and made annually great store of iron, good and merchantable, and sold it unto diverse men yet living at twelve pounds per tun.' Also 'all sorts of cast-iron wares, as brewing-cysterns, pots, morters, and better and cheaper than any were yet made in these nations with charcoles.'

But this success and cheerful working was only of short duration, for Dudley was again 'outed of his works and inventions' by the ironmasters and others wrongfully, and 'over long to relate'; but being unwilling that his inventions should 'fall to the ground, and be buried in him,' he commenced again 'at a furnace called Himley Furnace, in the County of *Stafford*, where he made much iron with pit-cole; but wanting a forge to make it into bars, was constrained for want of stock to sell the pig-iron unto the charcole ironmasters, who did him much prejudice, not onely in detaining his stock but also disparaging the iron; *Himley* Furnace being rented out unto charcole ironmasters.'

This furnace was given up, and Dudley erected a 'new large furnace on purpose, 27 foot square, all of stone,' at Hasco Bridge, Sedgley, with bellows of great dimensions, in which he made '7 tuns of iron per week, the greatest quantity of pit-cole iron that ever yet was made in Great Britain.' Near to this he discovered 'many new cole-mines 10 yards thick, and iron mines under it according to other cole-works; which cole-works being brought unto perfection, the author was by force thrown out of them, and the bellows of his new furnace and invention by riotous persons cut to pieces, to his no small prejudice and loss.'

This 'rattening' persecution seems to have quite broken him down for the time, as he speaks of himself as 'being with law-suites and riots wearied and disabled to

prosecute his art and invention at present even untill the first pattent was extinct.' During this period he was imprisoned for debt 'in the Counter in London,' but afterwards obtained a new patent, dated May 2, '*Anno* 14 *Caroli Primi* of ever Blessed Memory.' Dudley then made another effort, and, 'for the better support and management of his invention, so much opposed formerly at the Court, at the Parliament, and at the law,' he took into partnership with him David Ramsey, resident at the Court; Sir George Horsey, a Member of Parliament; Roger Foulke, 'a counsellour of the Temple and an ingenious man,' and also an ironmaster, who had been a neighbour, and 'one who did well know my former sufferings, and what I had done in the invention in making iron with pit-cole, &c.'

This firm was opposed 'by powerfull ironmasters with Sir *Philibeard Vernat*, a *Dutchman*, and Captain *Whitmore*, who pretended much unto his late Sacred Majesty, but performed not their undertaking.'

Dudley and his partners, in reply to this, petitioned the King; and at the Court of Greenwich, May 20, 1638, the petition was referred to 'Master Attorney and Master Solicitor General to call the petitioners before them, and to compose the differences between them; (if they can) or otherwise to certifie His Majesty their opinions therein; but Sir *Philibeard Vernat* and Captain *Whitmore* never appeared any more for their invention.'

Then came the Civil Wars, which caused the partners of Dudley to desist, and Dudley's own estate, for his 'loyalty unto his late Sacred Majesty and Master (as by additional Act of Parliament may appear) was totally sold.' Still he struggled on; or, to use his own words, 'I still endeavour not to bury my tallent, took in two partners into

my inventions, *Walter Stevens*, of *Bristow*, linnen draper, and *John Ston*, of the same city, merchant.' He then erected a new furnace near 'Bristow,' but this time fell into trouble with his partners, who, according to his own account, 'not only cunningly drew me into bond, entered upon my stock and work, unto this day detained it, but also did unjustly enter Staple Actions in *Bristow* against me, because I was of the King's party; unto the great prejudice of my inventions and proceedings, my patent being thus almost extinct; for which and my stock I am forced to sue them in Chancery.'

While this suit was pending, Cromwell and the Parliament 'granted a pattent and an Act of Parliament' to Captain Buck, of Hampton Road, giving him and his partners the exclusive right to make iron from pit-coal, thus overthrowing Dudley altogether. Dudley asserts, but without offering any evidence in proof, that '*Cromwell*, and many of his officers were partners, as Major *Wildman* and others; many doctors of physick, and merchants, who set up diverse and sundry works, and furnaces at a vast charge, in the Forest of *Dean*.'

All the efforts of these partners were failures. They used 'spacious wind-furnaces and pots of glass-house clay,' and having broken these, 'got unto them an ingenious glass-maker named *Edward Dagney*, an Italian then living at Bristow, who after he had made many potts and a new furnace, and made therein many sundry experiments and tryals,' failed in like manner, 'and his potts being all broken, he did return to *Bristow*, frustrate of his expectation.' But frustrate as he was, he promised further efforts, and obtained more capital from 'Master John Williams' and the master of Dagney's glass-house, who deposited 300*l.*; and when that was nearly exhausted in further failures,

they, hearing from Captain Buck and the other partners of Dudley's former success, 'importuned' him, 'at that time in great danger by the Parliament (being a colonel of the King's party), to go along with them into the Forest of *Dean*, which at that time he durst not deny. Coming thither, I observed their method of working, and found it impossible that the said *Edward Dagney*, by his invention, should make any iron with pit-cole or sea-cole in pots to profit.' Dudley remained with them until their pots were broken, and their capital was exhausted, and he tells us that 'at every dinner and supper' Captain *Buck*, Captain *Robins*, Doctor *Ivie*, Doctor *Fowler*, and others, would ask him 'why he was so confident that iron in quantity could not be made by their new inventions.'

They were evidently 'pumping' poor Dudley; but he was more than a match for them, and apparently put them on the wrong scent, for, after these convivial conferences, they made a further attempt, and, as he tells us, 'they desired me to come again a second time into the Forrest and see it effected; but at that time I saw their failings also.' But he did not set them right. Dudley gives no further particulars of this second visit and conference, but I suspect that he either accidentally or wilfully led them on a little farther, for they then erected new works 'at the City of Bristow, in which they did fail as much as their former inventions; but Major *Wildman*, more barbarous to me than a wild man, although a minister,' bought Dudley's estate (previously confiscated by the Parliament), 'intending to compell from the author (Dudley) his inventions of making of iron with pit-cole.'

It appears that this further effort to extort from Dudley his secret was also frustrated; and they afterwards 'passed' the estate unto two Barbarous Brothers of London,' that

pulled down his two 'mantion houses; sold 500 timber trees off his land, and to this day his houses are unrepared.'

In 1655, Captain Buck and his partners, 'wearied of their inventions,' finally gave them up, and in 1656 Captain John Copley obtained from Cromwell another patent. He and his partners 'set up their works at the Cole Works, near *Bristow*, and endeavoured by engeneers assistance to get his bellows to be blown, at or near the pits of cole.' But Copley, evidently an amateur iron-maker, failed even in the preliminary matter of getting wind from his bellows, and sent for Dudley, who 'told him plainly that if his bellows could have been blown by those engines' he could not make iron with pit-coal by the means he proposed. But Copley was not satisfied, or, as Dudley tells us, 'he seemed discontented; whereupon, and without those engines, I made his bellows to be blown feisibly, as by the note under his hand appears followeth.'

'1656, December 30.

'*Memorandum.*—The day and year above written, I, John Copley, of London, gent., do acknowledge, that after the expence of diverse hundred pounds to engineers, for the making of my bellows to blow for the making of iron with pit-cole and sea-cole, near Bristow and near the Forest of King's Wood; that Dud Dudley, Eqr., did perform the blowing of the said bellows at the works or pits abovesaid; a very feisible and plausible way, that one man may blow them with pleasure the space of an hour or two; and this I do acknowledge to be performed with a very small charge, and without any money paid to him for the same invention.'

Having made Captain Copley's bellows to blow 'feisibly,' Dudley left him to do the rest himself, in which, like the

others, he failed, and in 1657 gave up ironmaking altogether, and went to Ireland; 'and all men now desisting from the inventions of making iron with pit-cole and sea-cole, the author (Dudley), *Anno* 1660, being sixty-one years of age, and moved with pitty, and seeing no man able to perform the mastery of making ot iron with pit-cole and sea-cole, immediately upon His Sacred Majesties happy Restauration, the same day he landed, petitioned that he might be restored to his place, and his pattent obstructed, revived for the making of iron with pit-cole, &c., which said laudable invention the author was and is unwilling should fall to the ground and dye with him, neither is the mistery or mastery of the invention effected and perfected by any man known unto the author, as yet either in *England*, *Scotland* and *Wales*; all of which three abound with pit-cole and sea-cole, and do overmuch furnish other kingdoms many with pit-cole and sea-cole, when they might make far better use of it themselves, especially *Scotland* and *Wales*, both for the making of iron into cast works and bars, and also for the making of steel, and melting, extracting, and refining of lead, tin, iron, gold, copper, and silver, with pit-cole and sea-cole.'

This petition was rejected, and he petitioned again in 1663, when the consideration of his petition was referred to 'Master Atturney, or Solicitor General, or to either of them.' But, according to Dudley, these gentlemen 'would do nothing upon the reference,' and he petitioned again; and finally, in 1665, when sixty-six years of age, made his last appeal in the shape of the work above quoted, which, besides the history of his struggles and troubles, contains much sound, practical information concerning the geology of the neighbourhood of Dudley, so far as coal and ironstone are concerned. He describes the coal-

measures of this district as follows:—'The three uppermost measures are called the white measures, for his white arcenical, salsuginous and sulphurious substance which is in that cole; the next measure is the shoulder-cole, the toe-cole, the foot-cole, the yard-cole, the sliper-cole, the sawyer-cole, and the frisly-cole; these last three coles are the best for making of iron, yet other coles may be made use of.'

What, then, was the secret of Dudley's invention? may be fairly asked. This is not defined in the book. Inventors in those days were not compelled to explain their inventions intelligibly. Although the nature of Dudley's invention is not avowedly specified, I think I may base upon the general contents of the '*Metallum Martis*,' elucidated by what we now know concerning the manufacture of iron with 'pit-cole,' a 'feisible' hypothesis concerning Dudley's 'misterie or masterie.'

This is, simply, that he had no especial secret whatever beyond a sound, practical knowledge of the then established art of ironmaking with charcoal, and a certain degree of theoretical insight of the actions upon which the reduction of good iron depend, which enabled him to modify the furnace, the blast, and the charge, to select his ore and fuel, and to suit the varying conditions which were introduced by the use of the new fuel and reducing agent.

In the first place, he selected his ironstone skilfully and suitably, avoiding 'the sulphurious, arcenical, and veneriating qualities which are oftentimes in ironstone,' '*whose fiery quality is such that he will sooner self-calcine than separate from any sulphurious veneriated quality.*'[1]

[1] The italics are mine; their object is to direct the special attention of the reader to Dudley's clear understanding of a fundamental fact, that is still so seriously misunderstood in too many quarters, and on

Concerning the South Staffordshire ore he says :—'The first measure is called the Black-row graines, lying in very hard and black earth. The second measure is the Dun-row graines, lying in dun earth or clay. The third measure is called the White-row graines, lying in very white earth or clay; under these three measures are sundry other measures, and are called, first the Rider Stone; secondly, the Cloud Stone; thirdly, the Bottom Stone; fourthly, the Cannock, or Cannot-stone, which last may wel be so caled (although the other measures be very good), yet this stone is so sulphurous and terrestrial, not fit to make iron; because the iron thereof made is very redshare, which is that if a workman should draw or forge out a share mould fit for a plough in that red heat, it would crack.' He then describes 'the nature of cold-share iron, which is so brittle if made of the grain oare.'

In spite of his mystification of this part of the subject, it is evident that he understood that red-shortness is produced by sulphur, or connected with 'sulphurious veneriated' iron, and he rather vaguely connects cold-shortness with 'Arcenicall veneriated qualities.' This is curious when seen in the light of modern chemistry. We must remember that phosphorus was unknown in Dudley's time, and that chemical analysis can scarcely be said to have existed; therefore, much very shrewd practical observation was necessary in order to connect the red-shortness with sulphur. But the association of cold-shortness, which we now know to be produced by phosphorus, with arsenic,

which I have insisted repeatedly for some years past, as will be seen by what follows in the body of this book—viz., that neither phosphorus nor sulphur can be removed from iron by mere oxidation; that the iron itself becomes oxidised before parting with these impurities—'*will sooner self-calcine than separate from any sulphurious veneriated quality.*' As I show in subsequent chapters, a multitude of ingenious men have been ruined for lack of the understanding of this.

is still more remarkable—phosphorus and arsenic having some curious resemblances, especially in the garlic-like odour of their commonest compounds.

The ironstone that he describes as yielding cold-short iron is just that kind which exists in nodules with an organic nucleus, frequently containing phosphate of lime.

It is evident from the above quotation concerning the coal-measures, that his acquaintance with the composition of the different seams enabled him to select those containing the smallest amount of 'arcenical, salsuginous and sulphurious substance.'

The nearest approach to any definite secret appears to be that of coking, which he scrupulously omits to mention, though from his results, and his allusions to the economy of his invention in the utilisation of the then wasted slack, he must have used coke in his furnaces.

All the rest of Dudley's invention evidently depended upon the skilful management and adaptation of every detail of furnace-construction, of charge, of blast, and of final refining. In reference to this last element, he tells us that 'perfect tough malliable iron will not break feisibly in hot-heat or cold, as coldshare will, or red-hot as sulphurious veneriated red-share iron will; but yet tough enough when cold: all which aforesaid qualities of iron the authour very well knoweth how to mend their natures, by finning or setting the finery, "lesse transhaw, more borrow," which are terms of art; and by altering and pitching the works and plates, the fore spirit-plat, the tuiron, bottome, back and breast, or foreplate, by altering of which much may be done, if the work be set transhaw and transiring from the blast, the iron is more coldshare, lesse fined, more to the master's profit; lesse profitable to him that makes it into manufactorage, and less profitable to him that useth it;

but the iron made in a Burrow work, becometh more tough and serviceable.'

It is evident from this that careful refining of the pig, or an approximate puddling, by which the silicon and most of the carbon were separated from the pig, was an important element of Dudley's working.

If I am right in these inferences, the success of Dudley and the failure of his rivals is easily explained. He understood his business—they were mere amateurs. He solved the problem by skilfully adapting or modifying every stage or element of the process to the new conditions and requirements. They endeavoured to do it by the royal road of a special mystery or new device, such as using glass-makers' melting-pots, complex blowing-engines, &c.

His success and their failure are very instructive to all inventors, especially those who are sufficiently insane to believe themselves men of genius, and to suppose that the inspirations of genius can supersede the plodding industry which is necessary for the acquisition of technical knowledge and technical skill. Amateur inventors of the present day, and of all time, are, and have been, about as successful as were Cromwell's captains, the doctors of physick, the London lawyers and Bristow merchants, in their efforts to make iron from pit-cole and sea-cole in the seventeenth century. These rivals of Dudley are not the only inventors of their class who, 'after the expence of diverse hundred pounds to engineers for making their bellows to blow' 'feisibly,' have failed to raise the wind as they desired.

That Dudley clearly saw the possible developments of his invention in the district that has now become the 'Black Country,' is evident throughout his petitions, in all of which he exhorts the King to stop the exhaustion of the

forests, and to enable him to develop the mineral resources of the country. Speaking of the district around his own home —the country '*within ten miles of Dudley Castle*'—he says that 'God in His Infinite Goodness (if we will take notice of His goodness unto this nation) hath made this country a very granary for supplying iron cole and lime made with cole.' * * 'And not only this island, but also of his Majesties other kingdoms and territories with iron wares.' * * * 'Now if the coles and ironstone so abounding were made right use of, we need not want iron as we do; for very many measures of ironstone are placed together under the great ten-yards thickness of cole, and upon another thickness of cole two yards thick, not yet mentioned, called the bottom cole, or the heathen cole, as if God had decreed the time when and how these smiths should be supplyed, and this island also with iron; and most especially that this cole and ironstone should give the first and just occasion for the invention of the making of iron with pit-cole, no place being so fit for the invention to be perfected in.'

Anybody who has climbed the hill on which Dudley Castle is built, and looked from its walls or towers round upon the country lying within ten miles' radius, which, as Dudley tells us, 'did formerly abound in forrests, chases, parks and woods,' can appreciate the prophetic character of the above quotation. But the prophet was not honoured in his own country; he died in the midst of his petitioning, and his method of making iron 'with pit-cole, sea-cole, peat, and turff,' was buried with him, and remained thus buried for about a century, in the course of which the British production of iron and steel declined to less than three-fourths of its former amount. During all this time we were importing very dear iron and steel from Russia

and Sweden, and suffering the evils of disforesting, manufacturing depression, and the commercial disadvantages which Dudley so mournfully predicts in his petitions.

The subsequent development of iron and steel making, up to the Bessemer period, has chiefly consisted in rendering it possible to produce large quantities by making use of the more abundant and inferior raw material. Dudley's 3 to 7 tons per week indicates the scale of working then prevailing. The total produce of iron in Great Britain in 1740 was but 17,340 tons, all charcoal-iron still, Dudley's invention having been buried with him, and but gradually revived after that period.

In the *Philosophical Transactions* for 1747, the use of coal for iron-smelting is recorded as an exploit recently performed by Mr. Ford, who 'from iron ore and coal, both got in the same dale, makes iron brittle or tough as he pleases, there being cannon cast as soft as to bear turning like wrought iron.' As there is no record of Mr. Ford's invention in the Patent Office, we may presume that no patent was secured. The same applies to Darby of Colebrook Dale, who had already succeeded to some extent.

I should add that all the patents of his rivals referred to by Dudley in the *Metallum Martis* are officially recorded.

It was not until January 1783, and February 1784, when Cort's first and second specifications were filed, that the full effect of using pit coal and the ores associated with the coal was commercially felt. This rendered possible the practically complete elimination of 'the sulphurious and veneriated quality' of the crude iron made from these materials, by washing and wringing them out in the manner described in the subsequent chapter on Puddling. At the date of Cort's inventions, British production had reached to about 60,000 tons per annum.

		Tons			Tons
In 1788 we produced		61,300	In 1865 we produced		4,819,000
1796	„	108,793	1871	„	6,627,179
1806	„	250,000	1872	„	6,741,929
1820	„	380,000	1873	„	6,566,451
1827	„	654,000	1878	„	6,381,051
1845	„	1,200,000	1880	„	7,720,000
1851	„	2,500,000	1888	„	7,898,634

To understand the full signifiance of the utilisation of the inferior ores that are found in the same districts as the coal, we must remember the cost of carrying such materials at the time of Cort and his immediate successors.

Railways and steam-engines have recently effected another revolution in the conditions of iron-making. We are now returning half-way toward the ancient practices, by again using the richer and purer ores; are leaving in the ground the clay-ironstones described by Dudley, and importing rich hematites from Spain for the Bessemer process.

Among the reasons for the halt in our progress which occurred about 1872, is one that is seldom considered—viz., that iron, although subject to wear-and-tear and oxidation, is far from imperishable. Assuming, for example, that the average life of a rail is fifteen years, the millions of tons that were made from 1865 to 1872 must be thrown back as old iron between 1880 and 1887. Ship-plates, boiler-plates, shafts, girders, &c., come back, in like manner, as old scrap, and, the greater our production at the time of their birth, the greater their competition with new iron after death.

CHAPTER II

THE ORES OF IRON

THE sources of the metals are very variable. A few are found native, or reguline. This is usually the case with the 'noble' metals—*i.e.*, those which may be melted without loss of lustre or other metallic qualities. The connection between their nobility and this mode of crude existence is obvious enough. Metals that may be fused without oxidation are likely to remain metallic in the earth; while those with more active affinities naturally combine with neighbouring substances, especially if lying in those parts of the earth that at any time have been heated.

Silver, though one of the noble metals, readily combines with sulphur, and accordingly is found in the condition of a sulphuret, as well as in the noble or reguline condition.

Mercury, copper, and a few other metals not quite so aristocratic as gold and silver, are occasionally found in the reguline condition; but as we come down among the plebeian metals, we find them variously associated with their vulgar neighbours. Some are simply oxidised, many exist as sulphurets and carbonates, others are irregularly combined or mixed with a variety of earthy matters, such as alumina compounds, silica, &c.

These are variously distributed in veins, in nodules, or as strata forming massive rocks of varying thickness. The heavier of the common metals are most commonly

found in veins or fissures of massive rocks, where they have been deposited, either by eruption from below, or other obscure debateable actions that I cannot here discuss. This being the common condition of the sulphurets, opens up a very tempting field for speculation concerning the connection of metallic sulphurets with volcanoes and their other sulphurous accompaniments.

The lighter of the common metals that greedily hunger for oxygen, and whose oxides are earthy and strongly basic, or alkaline, are usually found combined with carbonic or silicic acid, forming massive rocks, such as our common limestones, slates, clays, &c.

Finally, those metals that form soluble alkaline compounds with oxygen are found most abundantly in saline combination, and dissolved in sea water or mineral springs. Such are sodium, potassium, lithium, magnesium, &c.

Iron is remarkable as existing in all these conditions, and being found everywhere. We cannot dig a spadeful of earth, or even a spoonful, in any ordinary ground, without finding sufficient oxide of iron there to render the whole mass of a deep blue colour when we add a little acid, and then some ferrocyanide of potassium (prussiate of potash). There is no geological formation on the earth that is free from it, and in most of them it is abundant. It is in the primary plutonic rocks, in their metamorphic neighbours, and in the sedimentary rocks of all ages. It is found in the metallic state: as oxide, as carbonate, as sulphuret; in combination and in admixture with alumina, silica, and all the chief materials of the earth. It is in the waters of the ocean, in mineral springs, in the blood of the higher animals, in the atmosphere around us, and in the heavens beyond. So rarely is it absent from any part of the earth, that a bed of sand free from iron is more

valuable than a gold mine; the glass-maker has great difficulty in obtaining supplies of such material. Clay free from iron is of similar rarity and value to the potter. The prevailing reddish-brown colour of the earth's crust is mainly due to iron.

This wide diffusion of iron is temptingly suggestive of a curious speculation,—viz., that it is due to meteoric iron-dust that has fallen from time to time upon the earth during all ages. Such iron-dust is mingled with the sand of the desert, on Alpine, Arctic and Siberian snows, on the upper ledges of the towers of the cathedral of Notre Dame in Paris, and other similar places. And, further, these particles of ferruginous dust, when examined under the microscope, prove to be little rounded globules, all of similar structure.

I have gathered snow that has fallen on my own garden, melted it, and examined the dark sediment left behind. In this I have found particles that jump to a magnet. Such ferruginous particles are continually falling on all parts of the earth, and by some are regarded as the material, or part of the material, of the so-called 'shooting-stars,' which are far more abundant than is commonly supposed. Whatever may have been the original dimensions of these meteors, the majority are pulverised as well as heated by the violence of their collision with our atmosphere. Professor Herbert A. Newton, in his address as retiring president of the American Association for the Advancement of Science, 1886, estimated the number of 'shooting-stars' that visit our earth at fifteen millions daily.

But I must now leave these speculations, and proceed to the practical part of my subject—to the ironmasters' raw material.

Here we again encounter mysterious visitors from

outside space, most of the known specimens of native metallic iron being, demonstrably, meteoric masses that have fallen on the earth at various times, and have been found resting where they fell. The stories concerning these wonders were disbelieved until the begining of the present century, when Sir Joseph Banks compared some specimens said to have fallen in Yorkshire, with others from Italy which were sent to him with similar accounts of their origin. All doubts were finally set at rest by the celebrated paper of Howard, published in the *Philosophical Transactions*, in 1802, accompanied with analyses of specimens from Benares, and followed the year after by a remarkable fall of similar stones in Normandy.

It is now clearly proved that they have fallen on all parts of the earth, and vary in size from the mere dust-grains above described to masses of many tons in weight. There is a fine collection of them in the British Museum, worthy of far more attention than it commonly receives, many visitors passing through the Museum without discovering that they are there at all.

The celebrated aërolite described by Pallas, who saw it in Siberia, weighed originally about 14,000 lbs. It was worshipped by the Tartars as a visitor from heaven. Another at Chaco, in South America, weighs about 30,000 lbs. Many of these contain from 80 to 90 per cent. of iron, 5 to 10 per cent. of nickel, and smaller proportions of cobalt. The occurrence of these three metals in most of the aërolites is a curious fact in connection with their magnetic properties; they have been called 'the magnetic triad.' If filings of all the metals were mixed together, a magnet would pick up those of the three celestial metals, and leave all the rest behind.

Other minerals—non-metallic — are found in some

aërolites. Thus, one of the above-named stones that fell at L'Aigle, in Normandy, was found by Thénard to contain :—

Silica	46 per cent.
Magnesia	10 „
Iron	45 „
Nickel	2 „
Sulphur	5 „

The Lenarto aërolite, which may be regarded as typical of the purely metallic class, was analysed by Werle, and found to be composed of:—

Iron	90·883 per cent.
Nickel	8·450 „
Cobalt	0·665 „
Copper	0·002 „

Graham found that, when a piece of this was heated to redness in a vacuum, it gave off 2·85 times its own bulk of gas, the greater part of which was hydrogen.

Besides the metallic iron found in unquestionable meteorites, small grains are found in basaltic rocks, imbedded there, apparently, when the rock was in a state of fusion, and protected from subsequent oxidation by this hermetical sealing. Such are found in the basalt of the Giants' Causeway, in Auvergne, &c. It is possible that these may be of meteoric origin, and have become entangled in the rock when it was in a state of fusion or semi-fusion.

Buttons of iron, combined with carbon, and described as 'native steel,' have been found in burnt coal-seams. A mass of such native steel, weighing 16 lbs., was found in such a coal-seam at Laborche, in the Department of Allier, in France.

There is no difficulty in explaining the origin of this. Many coals are what the miners describe as 'brassy'—*i.e.*, they contain iron pyrites, which has a golden-yellow

colour. I have seen a coal-seam, through the midst of which was a deposit varying from 1 to 8 inches thick, and composed of about half coal and half pyrites. If such a seam were fired underground, the pyrites would be reduced to a metallic-looking mass of very bad, crude iron, composed of sulphide and carbide of iron, which, being very hard, might be called 'steel' by a mineralogist, but not by a workman.

An example of recent and visible formation of such nodules came under my own observation a few years ago at Leeswood, in Flintshire. A large quantity of the rich bituminous shale, which underlies the cannel coal of that district, had been distilled for paraffin oil, and the residual coke formed an extensive spoil-bank, a long ridge by the side of the Coed Talon railway siding. This accumulation of stony and carbonaceous material became heated, and presently started into spontaneous combustion, which is a common occurrence in such heaps. Some time after the combustion had ceased, and the mass had cooled down, a working-man connected with the railway applied to the proprietors of the oil-works, and offered to carry away the spoil on very easy terms, if they would make a contract with him. This they willingly did, as they were in serious difficulties for want of space for the disposal of their continually-increasing accumulations.

His object in making the contract soon appeared. He had found amidst the burnt mass lumps of iron combined with carbon and silicon, having considerable value. It was, in fact, a sort of very crude pig-iron. When I was last there, a few years ago, he was struggling to remove a mass of this material, about as big as the body of an elephant, which had already been laid bare by the removal of the friable material around it.

But I must now pass from these mineralogical curiosities

to the compounds which constitute the ores that are practically worked on a large scale. The best and richest of these are the oxides, some of which are pure, others mixed with more or less of foreign matter. Of course, the pure oxides are best of all. I say 'oxides,' not oxide, because iron combines with different proportions of oxygen. There is the protoxide of iron, composed of one equivalent of iron and one equivalent of oxygen. Those who have studied chemistry, well know that this means fifty-six parts by weight of iron to sixteen parts by weight of oxygen, the atomic or equivalent weight of iron being 56, and of oxygen 16. This oxide, therefore, contains nearly 78 per cent. of pure iron; but it is not found native, though easily formed in the laboratory.

There is an intelligible reason for its scarcity as a mineral—viz., that this protoxide, especially when hydrated, or combined with water, greedily combines with more oxygen, and thus may become a higher oxide, called the sesquioxide, composed of two equivalents of iron to three of oxygen, and therefore containing 70 per cent. of iron. But this change only occurs fully when there is a plentiful supply of oxygen and a moderate temperature. If there is a stint of oxygen, or high temperature, an intermediate oxide is formed, by what appears to be a combining of the sesquioxide with the protoxide. This is the 'magnetic oxide,' composed of three equivalents of iron to four of oxygen, and therefore containing above 72 per cent. of iron. There is still another oxide, called ferric acid, composed of one equivalent of iron to three of oxygen. Thus we have—

Protoxide	(FeO)	containing	nearly 78	per cent.	of iron.
Magnetic oxide	(Fe_3O_4)	„	above 72	„	„
Sesquioxide	(Fe_2O_3)	„	„ 70	„	„
Ferric acid	(FeO_3)	„	nearly 54	„	„

The first and the last of these may be dismissed from present consideration, as neither of them form ores that are practically worked.

The richest of all iron ores is, therefore, THE MAGNETIC OXIDE, containing, when pure, above 72 per cent. of metallic iron. In its purest natural state it is the famous '*loadstone*,' or leadstone, which is sometimes found as dark, iron-grey, cubic or octahedral crystals, that are polarised, or actively magnetic. In other cases it is passive —*i.e.*, may be attracted by an active magnet, but has no active powers by itself. It more commonly exists in granular masses, the crystalline grains of which are more or less mixed with foreign matter.

It is found in the older rocks—the primary and metamorphic—which contain no organic remains. Very little is obtained in this country. It is especially abundant in Sweden, Norway, and Lapland; also in the Ural Mountains, in Piedmont and Saxony, and other countries where there are mountains formed of the older rocks.

This is the ore that was used by the primitive iron-makers, and it is still worked in countries by the primitive methods, which simply consist of mixing small fragments of the oxide with charcoal, heating them together on a rude hearth, or in a small clay chamber, and using a blast to raise the temperature as high as possible.

The ores which are next in richness and purity to the magnetic oxides are the sesquioxides, (F_2O_3), containing about 70 per cent. of iron when pure. They are found in various forms—crystalline, massive, pulverulent, earthy, and reniform, or kidney-shaped, as in the so-called 'kidney ore.' A general name of 'RED ORES,' or 'HEMATITES' (Gr. *hæma*, blood), is given to them on account of their colour. Some of the hematites are so soft in

structure that their particles rub off, and stain the fingers with an unctuous smear, like black lead; but the colour is red.

As they usually contain more or less of siliceous, calcareous, and other impurities, 60 to 65 per cent. of iron may be regarded as a fair proportion for a rich commercial sample.

When the soft variety occurs interstratified with a limestone rock, it is sometimes very deceptive. As an instructive example, I mention a case that came under my own notice. A friend had purchased the working-lease of what appeared a splendid deposit of hematite in the Vale of Clwyd. He sent out samples for analysis, and the results were highly satisfactory. Upon these samples he obtained orders from an ironmaster in Denbighshire, and the ore was charged into the furnace mixed with commoner ores. The yield of the furnace immediately declined, and further supplies were refused.

Shortly after this I visited the deposit, and upon careful examination found a thick face of bright red rock fully exposed, which was said to be the face of a solid deposit of hematite. It appeared to be such at first sight. On careful examination, I found that the bulk of the deposit was merely a porous limestone, deeply stained throughout by red oxide of iron—which had apparently been deposited simultaneously with the carbonate of lime—and that here and there were strata of true hematite, varying from mere laminæ to layers of a few inches thick. In these places the hematite was soft, nearly pure, and easily removable. It was evident that the samples had been taken from these strata, while the bulk delivered to the ironmaster was an average of the whole deposit, and therefore chiefly composed of merely a stained limestone.

Hematites are more abundant than the magnetic oxide. The most important British deposit of this ore is in the neighbourhood of Ulverstone, in Lancashire. Near Cleator Moor it varies from 15 to 60 feet in thickness, and is of very fine quality, being especially free from phosphates, and therefore in great demand for the manufacture of Bessemer pigs, of which hereafter. Similar ore is found on and near the coast of Antrim, in Ireland, and has been supposed to extend under the sea lying between.

Vast deposits exist in the neighbourhood of Bilbao, in Spain, and some English and Spanish capitalists are working it there. They have their own railways from the mines, or rather quarries of the ore, to the coast, and suitable steam-vessels for bringing it across.

It is also abundant in America, especially on the shores of Lake Superior. The Iron Mountain and Pilot Knob, near St. Louis, in Missouri, are celebrated for this ore.

Its freedom from phosphates is due to its geological position. The phosphates which are so damaging to the clay ironstones are mostly, if not entirely, due to the remains of vertebrated animals, whose bones contain so much phosphate of lime. The nucleus of many of the clay ironstone nodules is a fossilised fish. The best hematite occurs chiefly in the Cambrian and Silurian rocks, in which are only the remains of invertebrate animals, whose solid framework is carbonate of lime. Some is found in the Devonian, where the early dawn of fish-life appears.

There are also deposits in the carboniferous limestone, but these are not usually of the best quality.

SPECULAR IRON ORE (not to be confounded with spiegeleisen, which it resembles both in appearance and etymology) is another variety of anhydrous sesquioxide of iron found in volcanic districts. It is in hard, crystalline,

mirror-like plates, hence its name. It is probably formed by the action of volcanic heat upon hematite. The Elba deposit is one of the most famous.

ROUGE is an artificial sesquioxide prepared by roasting the sulphate of iron (green vitriol) at a red heat. I merely name it in passing, as its uses for polishing glass and jewellery, and as a pigment, are not strictly metallurgical.

IRON-SCALE, or scale oxide, requires further description, inasmuch as it is an important material in practical metallurgy, doing the work of an ore, although an artificial product. It appears to be a compound of the protoxide with the sesquioxide; its composition, however, is variable. The outer surface of the scale, when thick, and the result of long exposure of the iron to heat, is of nearly the same composition as the magnetic oxide, but the inner layer has a composition varying from 4 FeO_4, Fe_2O_3, to 6 FeO_4, Fe_2O_3. It all has similar magnetic properties to the magnetic oxide.

There is another set of sesquioxides differing from the above by containing water in combination. This must be distinguished from the water which adheres to the ores, and which, although accidental, is not unimportant. A hundredweight or more may easily be added to a waggon-load of pulverulent hematite by merely leaving it exposed in wet weather. This, however, being merely held mechanically, is driven off as vapour by simply heating to the boiling-point of the water. That in chemical combination forming the hydrate, requires roasting at a red heat to get rid of the water. Ordinary iron rust is a hydrated sesquioxide, which may be converted into rouge, or anhydrous sesquioxide, by such roasting.

The most important of the natural hydrated sesquioxides are the BROWN HEMATITES. Brown ores and

limonite are names also applied to the same. They vary greatly in structure and purity: some are hard and compact, with no particular structure; others are similarly hard, but on fracture present a fibrous structure, really due to crystallisation. Others, again, are ochreous, earthy, and yellow-brown. These are the more common, and they contain the largest amount of siliceous and clayey impurities. The rich brown, hard, and pure varieties may rather be regarded as museum specimens than ordinary ores available in quantity for practical working.

The practical metallurgist should always bear in mind when he visits a museum that the curators of these establishments, and mineralogists generally, care more for rare than for common specimens, and therefore museums generally are by no means representative of natural distribution. It would be well if, in our geological and mineralogical museums, we were to have a *vulgar department* in which ordinary specimens of average imperfect fossils, average ugly minerals, average ores, &c., were shown for the benefit of the student, who might thereby be taught to recognise what he is most likely to pick up as specimens, or have to use in practical work.

In spite of the varieties of form of both the anhydrous and the hydrated hematites, they may be distinguished by a very general and easily-applied test—viz., the streak. Whatever be the colour of a tolerably hard piece of anhydrous hematite ore, it will show a red mark or streak if scratched by something harder than itself. On the other hand, the hydrated hematites display a brown streak. A penknife-scratch is all that is necessary for showing this. The most important of our British brown hematites are those of Northamptonshire and the Forest of Dean. The latter were worked by the Romans, and the remains of

their furnaces and cinders are yet visible. Brown ores are largely used by the Belgian and French ironmasters.

There is a curious variety of the hydrated sesquioxide found in bogs, especially in those bogs which occupy the sites of former lakes, or where pools formerly existed, or still exist. It is called BOG ORE, and abounds in Sweden, Norway, Finland, Holland, and North Germany. In the Irish bogs it is found in pockets, or agglomerations, here and there, and is picked out by the peasants, and put in heaps on the roadside, to be collected and shipped to London, &c., for the purification of coal-gas. Considerable quantities are thus obtained from the wild regions of Donegal, near to the coast of its beautiful estuaries. In the lake region surrounding the Baltic, the Gulf of Finland, and the Gulf of Bothnia, it forms strata of considerable extent.

Its origin was once a mystery, but is now explained. Microscopic creatures, formerly described as animals (*naviculæ*), but now known and classed in the Vegetable Kingdom as *diatoms*, have assimilated the iron dissolved in the bog water, and have combined it with the material of their cases or skins; these locomotive vegetables have died generation after generation, and thus have deposited this oxide, together with much silica.

The silica renders the iron made from this ore readily fusible, and beautiful castings for brooches and other ornaments, vying with lacework in delicacy, have been made. Between thirty and forty years ago these bog-iron ornaments were in active demand, so much so that there were shops devoted especially for their sale. I remember one in Edinburgh (Müller's), where exquisite specimens were displayed. But fashion, ever capricious, has now dropped them, and they have become museum curiosities.

FRANKLINITE, found and worked in New Jersey,

is a mixture of the oxides of iron, zinc, and manganese. Rammelsburg's analyses show an average composition of:—

Iron	45·16 per cent.
Manganese	9·38 „
Zinc	20·30 „
Oxygen	25·16 „
	100·00

It is worked, primarily, for the zinc in conjunction with the deposit of red zinc ore which overlies it, and the residue of iron and manganese is made into spiegeleisen. Some of the metallic 'Yankee notions' offered for sale in this country are made from the hard and brittle cast iron obtained from this mineral. Steels for knife-sharpening, cheap pencils sold for glass-cutting, consisting of a fragment mounted at the end of a stick, may be named as examples. The oxide of iron in this ore resembles in composition that already described as iron-scale. It is feebly magnetic; theoretically, a compound of 3 FeO, Fe_2O_3.

ILMENITE is abundant in Norway, where it forms masses of dense, dark, iron-grey rock, of granular and somewhat micaceous, or glistening structure. It is composed of protoxide and sesquioxide of iron, with varying quantities of titanic acid and magnesia. The IRON SAND found at Taranaki, in New Zealand, and in the Bay of Naples, is composed of siliceous particles mixed with darker grains that are separable by the magnet. They have a similar composition to ilmenite.

Good specimens of these oxides are workable by the primitive methods above referred to, nothing more being required than to drive off the water in the hydrated kinds, and bring the anhydrous oxides into contact with heated charcoal, when the simple reductions already described

take place, forming either spongy iron or fluid steel. It is notable that these materials of the primitive iron-workers belong geologically to the similarly primitive rocks.

As these old rocks were worn away by dashing waves, by roaring torrents, and grinding glaciers, and their pulverised fragments were carried down into the still waters, to be there deposited, and form the sedimentary rocks of a later age of the world's growth, the ferruginous particles of the original rocks were exposed to the reducing action of vegetable and animal matter in the course of decomposition. Such reducing agents, acting in the humid way, are not competent to effect the complete reduction of sesquioxide or magnetic oxide into metallic iron; but, as the experiments of Bischoff have shown, they do effect a reduction from the sesqui- to the protoxide. But what will happen at the same time ?

A little reflection on the well-known chemical relations of such substances will enable us to answer this question, and, I believe, correctly. The decaying organic matter gives out carbonic acid; the protoxide of iron is a base that readily combines with this acid, and thus carbonate of iron must be formed under such conditions. This theory is verified by a worldwide array of facts. In the later geological formations, where the remains of animal and vegetable life abound, the ironstones are carbonates, instead of oxides, as in the older rocks; and these carbonates are associated with other materials, the necessity of removing which has built up the art and science of the modern ironmaster.

THE CARBONATES OF IRON (FeO, CO_2) would, if pure, contain about 49 per cent. of metal; but samples of such richness are rather to be regarded as museum specimens than as ores for practical working. The nearest

approach to such purity among the practical ores is found in some of those known as 'SPATHIC IRON ORES,' or 'spathic carbonates' (the term 'spathic' is of German origin, and means sparry, the ores being so named from their structure and appearance). The following analyses show the composition of some characteristic Continental specimens:—

	1	2	3	4	5
Carbonate of iron . .	88·98	83·03	81·0	72·31	77·23
Carbonate of manganese .	4·86	6·07	13·0	16·67	15·37
Carbonate of lime . .	2·23	0·89	3·5	1·78	—
Carbonate of magnesia .	—	1·57	1·5	3·36	6·55
Peroxide of iron . . .	—	4·10	—	—	—
Gangue	—	—	1·0	4·20	—
	96·07	95·66	100·0	98·32	99·15

No. 1 is iron spar from Dankerode (Lower Hartz), analysed by Klaproth. No. 2, by the same, is iron spar from Kemlas (Bayreuth). No. 3 is pale yellow iron spar from St. George de Huntières (Savoy), analysed by Stromeyer. No. 4 is iron spar from Stahlberg, near Siegen, analysed by Bertha. No. 5 is white iron spar from Stahlberg, near Müsen, analysed by Magnus. All are selected from a large number given in vol. iii. of Bischoff's *Chemical and Physical Geology*. The manganese in all of them is a characteristic constituent, the importance of which will be discussed when I reach the subject of Bessemer steel and spiegeleisen.

These ores occur most commonly in the Devonian rocks; some are found as early as the Upper Silurian, and others as late as the Permian—*i.e.*, they occur generally at about the time when the vertebrated animals made their first appearance.

This is a fact of some practical importance, as the framework of the animals preceding the vertebrata was composed of carbonate of lime, while the bones of the vertebrates contained phosphate of lime; and the carbonates of iron, being more or less associated with organic matter, the beginnings of the appearance of that troublesome impurity, the phosphorus, is connected with geological age. The Devonian rocks, however, only show the crude beginnings of vertebrated animals in the form of odd fishes with soft cartilaginous, half-and-half sort of bones, and accordingly only mere traces of phosphorus are found in these carbonates.

Spathic carbonates are not abundant in Britain; our principal deposits are those of Weardale in Durham, Perran Arworthal in Cornwall, some at Exmoor in North Devon, and Brendon Hill in Somerset. The following are analyses: (1) the Weardale, by Dick; (2) the Brendon Hill, by Spiller:—

	1	2
Protoxide of iron	49·47	43·84
Protoxide of manganese	2·42	12·64
Peroxide of iron	—	0·81
Lime	3·47	0·28
Magnesia	3·15	3·63
Carbonic acid	37·71	38·86
Phosphoric acid	trace	—
Silica	4·93	—
Bisulphide of iron	0·08	—
	101·23	100·06
Metallic iron	38·56	34·65
„ manganese	1·86	9·73

These analyses are stated in a different manner from the preceding, but may be rendered comparable by adding

to the protoxides of iron and manganese their respective shares of the carbonic acid, or by taking the carbonic acid away from the others.

The Stahlberg, or steel mountain, near Müsen, in the Devonian rocks of the Rhine, is one of the most celebrated of the Continental deposits. A wedge-shaped lode in the clay slate has there been worked for more than five and a half centuries, and yields above 30,000 tons per annum. The Erzberg, or ore mountain, in Syria, is still more productive, producing above 110,000 tons per annum. Spathic carbonates are widely distributed in other Continental localities.

The argillaceous carbonates of iron, or CLAY-IRONSTONES, are the most abundant and important of British iron ores. They are the poorest and most impure of all the ores that have ever been practically worked, and owe their importance to their proximity to great coal-beds. This association of impurity with convenience of position is no mere accident—not a matter of geological good luck or ill luck—but a geological necessity. When the coal was formed, the earth had reached a period of its growth when organic life was abundant, and when turbid rivers and rivulets were forming abundant deposits of mud and clay.

The iron there deposited no longer appears as mere oxide, but, besides being combined with one of the results of the decomposition of organic matter—viz., the carbonic acid—the carbonate thus formed is more or less commingled, mechanically, with the clay and mud—the dirt of the period. Thus, we have in these ores carbonate of iron mixed with silica, alumina, lime, magnesia, phosphates and sulphates of lime, &c., water, organic matter, and other minor impurities.

The coal-seams themselves are remarkably free from earthy impurities and animal remains, showing that they must have been deposited in clear water, and not, as some geologists imagine, at the mouths or deltas of great rivers. If so, they would be loaded with mud. The clay-ironstones are *near* the true coal, *but never in it.* Iron is found in the midst of coal, but it there exists in the form of bisulphide, or iron pyrites—those golden-yellow crystals that have been actually collected as gold. The 'brassy' coals are those in which the pyrites is deposited so abundantly as to damage, and in some cases ruin, the value of the coal.

The clay-ironstones do not occur in veins, but as stratified deposits, and in nodules. The veins which commonly contain the ores of the other useful metals strike through the surrounding strata quite unconformably and independently of the general order of deposition. They appear to be fissures in the original rock, somehow filled with the metallic ores by some subsequent action, and apparently from below upwards.

The clay-ironstone is different—it is rock-matter itself, has generally a compact stony structure, and varies in colour from grey and yellowish to light brown, dark brown, slate colour, and black, with intermediate shades. The grey varieties commonly change to brown upon exposure to the air. This is due to oxidation, some of the superficial carbonate being decomposed, and converted to sesquioxide. All the clay-ironstones indicate by their structure that they have been deposited from water.

The nodules are found in the shales and clayey rocks of the coal-measures, and in later formations. They are in some places so close together as to form beds, in others at varying distance apart. Many of them have a nucleus in

which can be traced the remains of a fish, or of crustaceans, shells, or plants. These usually contain the largest proportions of phosphoric acid. The great coal-fields of North and South Staffordshire, Yorkshire, Shropshire, Derbyshire, South Wales, Denbighshire, and Scotland have an abundance of clay-ironstone, while little is found in the Lancashire and Durham basin.

The following analyses show the heterogeneous composition of these ores. The 1st is the main seam at Eston Nab, Middlesbrough, by Crowder; the 2nd, another Cleveland ore, by Dick; the 3rd, fire-clay balls, Dudley, South Staffordshire, by Dick; the 4th, Dale Moor rake, Stanton, Derbyshire, by Spiller; the 5th, White Flats ironstone, Shropshire, by Spiller:—

	1	2	3	4	5
Protoxide of iron . .	43·35	39·92	47·87	39·55	44·33
Peroxide of iron . .	1·20	3·60	—	2·71	1·06
Protoxide of manganese	—	0·95	1·12	1·50	1·00
Alumina . . .	9·88	7·86	0·43	1·14	0·92
Lime	0·58	7·44	1·00	3·32	2·86
Magnesia . . .	5·35	3·82	1·27	2·85	1·97
Silica	7·65	7·12	—	—	—
Carbonic acid . .	22·96	22·85	30·96	28·63	30·92
Phosphoric acid . .	3·87	1·86	0·07	1·12	0·70
Bisulphide of iron .	0·09	0·11	0·25	0·05	0·07
Water	5·07	2·97	1·18	1·75	1·30
Organic matter . .	—	—	0·41	1·14	0·48
Insoluble residue . .	—	1·64	15·95	15·80	14·35
	100·00	100·14	100·51	99·56	99·96
Metallic iron . .	34·54	33·65	36·56	33·20	35·61

The insoluble residues of Nos. 3, 4, and 5, are largely due to the silica not separately determined. The large percentage of phosphoric acid in the Cleveland ores should be noted.

It has rendered the pig-irons of that district, and also the Stanton pigs, about the worst in the market; but, as we shall presently see, this impurity, and the difficulties it presented, has stimulated the efforts of inventors and iron-masters, and thereby is actually adding to the prosperity of the district. The same was the case with the sulphur in the Staffordshire ore at an early date.

Those who believe that the manufacturing prospects of a people depend upon natural physical advantages, should reflect upon the fact that the greatest ironmaking districts of the world are those supplied with the worst and poorest ores, and that the most important improvements in the manufacture of iron—in fact, all the modern progress that has been made in this great branch of manufacture—has been the result of struggles against the difficulties presented by these impurities, and those of the fuel which is used in smelting the ores and working the iron. Where the ores and fuel are rich and pure, primitive methods still prevail.

The workable thickness of the Cleveland beds reaches to 17 feet, and their average yield amounts to about 20,000 tons per acre. They are above the coal-measures in rocks of much later date than the Carboniferous, and this is doubtless the cause of the great percentage of phosphorus they contain.

I have said that clay-ironstone is not found deposited in the coal-seams themselves. There is, however, an apparent exception to this presented by the ore next to be considered—viz., the BLACKBAND IRONSTONE, in which we find coaly matter and clay-ironstone intermingled. This is not a case of ironstone deposited in coal, but of bituminous or carbonaceous matter filling up the pores of an ironstone rock. This carbonaceous matter

is not exactly identical with ordinary coal, but more nearly resembles cannel coal, its chemical composition and physical condition being almost, if not quite, identical with that of Boghead cannel, or the bituminous shales of the neighbourhood of Bathgate, Scotland, and those which underlie the Flintshire cannels.

The composition of blackband ironstone corresponds to that of a rich sample of clay-ironstone, or spathic carbonate, plus 15 to 25 per cent. of bituminous matter—quite sufficient to serve as fuel for its own calcination, which is effected by simply burning it in heaps, when it leaves behind a rich, roasted ore, from which the carbonic acid has been expelled. Its composition and value were discovered by David Mushet, in 1801, but it was not fully worked until 1830. The supply is now falling off, for, although it extends over large areas, its thickness is very irregular, and usually not sufficient to pay for working. One of the largest and best-known deposits is that of Airdrie. It is found in workable seams in North Staffordshire, and in thin strata in most of our coal-fields; also in the Rhenish, Westphalian, and other Continental coal-fields.

IRON PYRITES, the bisulphide of iron, $Fe S_2$, is unimportant from a metallurgical point of view, as it is used for the sulphur it contains rather than for the iron. Even after the sulphur is so far roasted, or burnt out, as in the manufacture of sulphuric acid, the quantity still remaining with the residual oxide destroys its value as a source of metallic iron. Many attempts have been made to utilise it for this purpose, but with little or no success. It is better suited for the production of salts of iron than for the metal itself.

Deposits of iron ore are more abundant than is gener-

ally supposed. In order that they shall pay for working, something else besides thickness and richness is required. They must either be near to coal or wood supplies, or to roads or water-carriage, by which they may be cheaply conveyed to the coal. The ore must be carried to the coal rather than the coal to the ore, simply because, generally speaking, the weight of coal required per ton of iron produced exceeds the weight of ore required. The richer ores, alone, are worth carriage to any considerable distance. Poor ores are only worth working when close to the coal.

Such has been the case hitherto, but there is a possibility of some change in the future. Every great improvement in the manufacture of iron diminishes the quantity of coal required per ton of given quality of ore; and thus we are continually approaching the possibility of finding it cheaper to carry coal to certain ironstones than the ironstone to the coal. When this is reached, serious changes may occur. They would, probably, have occurred ere this but for the interference of legislators, who have not yet learned that free international competition determines by natural selection the most advantageous course of industrial evolution, by directing the capital of each country into those investments which develop most effectively its peculiar natural resources.

Our ironmasters will do well to remember that the resources of the United States, and of some of our colonies, in respect to the raw materials of iron-making—the ores and coal—are vastly greater than ours; while, on the other hand, our climate, our labour-supplies, and general concentration of population, afford us unmistakable advantages in the production of finished iron and the more highly-elaborated products of which iron and steel are the materials.

When the American capital which has been forced by

legislative violence into this latter direction is allowed to stand on its own legs, and to move freely and vigorously, it will put an end to our export trade in such crude material as pig-iron, rails, &c. The utmost demand upon our blast furnaces, Bessemer converters, &c., will then be to supply the pig-iron and crude steel required for our home manufactures of machinery, hardware, cutlery, and other elaborations of raw metallurgical material, in the production of which we may continue to excel, in spite of the increasing scarcity of our coal-supplies and the inferiority of our iron ores.

Some of us may even live to see the time when pig-iron will be shipped from America to this country as ballast, as wheat is being shipped at present.

CHAPTER III

REDUCTION AND DISSOCIATION

As I shall require continually to use the terms 'reducing' and 'reduction,' let us start fairly with a clear understanding of their meaning when used as metallurgical technicalities. This is obviously very different from their ordinary meaning. The discovery which laid the foundation of modern chemistry was that of oxygen, by Dr. Priestley, and his experiment affords a beautifully simple example of metallurgical reduction.

It is the experiment which he is represented in the act of performing by that admirable portrait-statue near the Midland Institute, Birmingham. He had already observed that, when the red oxide of mercury is heated, it loses its red colour, and the powder becomes converted into small globules of metallic mercury. But what happens besides this change? Is something added, or is something taken away?

The general chemical theory which then prevailed, asserted that all combustible substances were composed of a basis of some sort, combined with a fiery principle, which was named 'phlogiston,' and that, when these substances were burned, the fiery matter was driven out, or they became 'dephlogisticated.' What we now call the oxides of metals were named the calxes, or earths of metals; and seeing that iron, for example, when burned, became con-

verted into such a calx, or earthy substance, these calxes were described as dephlogisticated metals.

A serious blow had already been dealt to this theory by Dr. Black, who weighed a piece of iron, then burned it carefully, and weighed the result of its supposed dephlogistication. Instead of losing anything, he found that it had gained—was considerably heavier. To this the phlogiston theorists replied that phlogiston, or the fire principle, was ethereal; that it gave lightness to bodies—was spiritual rather than material. A crushing rejoinder to this was supplied by the experiment of Priestley; he proved that, instead of something being taken from the metal to produce the calx, there was something in the calx, the removal of which produced the metal, and that this something was the wonderful gas which we call oxygen.

His experiment was very simple and demonstrative. He placed some heavy, red, scaly powder, then called the calx of mercury, in a tube closed at one end, then filled the tube with metallic mercury, and immersed its mouth in a vessel of mercury, thus leaving the inverted tube filled with metallic mercury, on the top of which floated some of the red calx. He then heated this calx, while still within the tube, by means of a lens, or 'burning-glass,' which he held at the distance required to bring the focus of the lens, where the sun's rays concentrate, directly upon the red powder. The heat thus applied converted the red powder into metallic mercury and a gas which gradually filled the tube. This gas was oxygen.

In this experiment we have the simplest case of reduction of a metal from its oxide, which reduction is the removal of the oxygen and liberation of the pure metal. The term is also applied, though not so uniformly, to the

separation of sulphur from the sulphides of metals—as when copper is obtained from copper pyrites, which is a sulphide, or when lead is smelted from galena, also a sulphide. The oxides of gold, silver, and platinum, may be reduced by simply heating them; they are even more readily reduced than the oxide of mercury.

Everybody knows that we cannot thus easily reduce the oxide of iron; that, on the contrary, the simple heating of iron in the air causes it to combine with oxygen, to form a black scale, which is one of its oxides. No amount of heat will thus effect the oxidation of gold, silver, or platinum. This fact, which was well known to the old alchemists, led them to designate these as the 'noble metals.' Mercury is curiously intermediate, and apparently contradictory. If moderately heated in the air, it combines with oxygen, and forms the red oxide; this oxide, when made still hotter, gives off the oxygen thus obtained, and the bright metal returns. Lavoisier followed up the work of Priestley by thus adding oxygen to mercury, and then taking the same away. By this and other demonstrations of oxidation and reduction he demolished phlogiston.

I select this example, not only on account of its simplicity and classic interest as connected with the past history of chemistry, but as affording a typical illustration of the most recently demonstrated, and, to the metallurgist, the most important of the great general laws of modern chemistry—viz., the laws of dissociation by heat. They constitute the fundamental basis of the philosophy of all smelting and ore-reducing, and should be understood by every practical metallurgist.

What is heat? This question has been often asked, and variously answered. It was formerly supposed to be a subtle fluid, without weight, but having the power of

penetrating ponderable bodies, and exerting an expansive or repelling force upon their particles. It was called *caloric*, and there are people still among us who imagine they display superior learning by using this word instead of heat; but in doing so they exhibit the contrary, as caloric has now gone the way of phlogiston, and heat is regarded by those who best understand the subject as a state or affection of matter—an internal movement, which displays itself most generally as repulsive energy, effecting expansion, and exciting in animals the sensation of warmth.

This repulsive energy is exhibited in three ways:—(1) By simply increasing the bulk of the heated body. (2) By overcoming the cohesion of its particles, and changing its state and form, as from solid to liquid, and liquid to gas. (3) By altering its composition. This latter is dissociation, and recent researches indicate that it is as universal an effect of heat as fusion and evaporation; that there is no chemical compound, however stable it may appear to be, that can resist the separative energy of heat, provided its temperature be sufficiently raised.

The analogy of dissociation to evaporation is remarkably close. To illustrate this I will take the case of water, which, as all my readers know, is a compound of hydrogen and oxygen united by the most powerful of chemical ties, and therefore one of the most stable of chemical compounds.

When water is heated to a certain temperature, it 'boils'—*i.e.*, it is converted into steam, or gaseous matter, but not all at once. We must not only raise the water to the boiling-point, but we must continue the application of heat—*i.e.*, supply more and more heat—in order to keep up the boiling. If this were not the case, the boiling of a pint of water would be a very dangerous operation. If it all became steam a once when raised to its boiling-

point, a terrible explosion would occur, as water in becoming steam expands to 1,700 times its liquid bulk. Water would thus be far more dangerous than gunpowder, seeing that gunpowder must be raised to 600 degs. before it becomes gaseous, while water becomes a gas at 212 degs.

This slowness of the outflying or evaporation of the water is due to the well-known fact that the work of converting the liquid into gas renders a certain amount of heat 'latent'; or, more philosophically speaking, a certain amount of heat-force ceases to display itself as temperature, being otherwise occupied—*i.e.*, in doing the work of gaseous expansion, or conferring upon the water that internal repulsive energy which is the physical characteristic of the gaseous state of matter. The amount of heat which thus disappears in boiling under ordinary circumstances is equal to that which would raise the water, if still liquid, 990 degs. This is carried off by the steam; hence the apparent paradox of water remaining at the same temperature in spite of continual application of more and more heat.

If we now proceed further, and continue raising the temperature of the steam, we shall at last reach a point at which its elements will be driven asunder. This temperature is so high that it cannot be accurately measured; it is about 5,000 degs. Fahr., or near to the melting-point of platinum.

But it is not sufficient merely to thus raise the temperature; this is only the starting-point. For the work of dissociation to go on, a continuous application of heat is necessary, just as in the case of boiling water. The amount of heat demanded to do the work of tearing asunder the chemical bonds of hydrogen and oxygen is equal to that

which would raise the steam 8,000 degs. above the high temperature of the dissociation-point. This amount disappears as temperature, is rendered latent in the act of dissociation.

From this follows another law—viz., that the amount of heat thus rendered latent in the act of dissociation is given out again by recombination. The analogy of this to the case of steam is at once obvious. When steam is condensed into water, the 990 degs. that disappeared in boiling reappear as temperature. If we blow 1 pound of steam at 212 degs. into 991bs. of water at 202, the water will all be raised to 212 degs., the material of the steam remaining unchanged in temperature, but transformed into liquid water, of which there will now be 1001bs., all at 212 degs.

The chemical recombination, so strictly analogous to condensation, is neither more nor less than ordinary combustion. Our fires, our candles, our gas-lights, &c., in their burning afford familiar, but little understood, examples of this restoration of the latent heat of dissociation. When we burn coal we are restoring the sunbeams that have been bottled up and buried in the earth during thousands and tens of thousands of years. These sunbeams, by the agency of the living plant, dissociated the carbonic acid and aqueous vapour of the atmosphere of the ancient world, and, by burning the carbon and hydro-carbons of the coal, we restore these compounds to our modern atmosphere, as well as the old buried temperature.

This brings us to another law of dissociation. It is quite evident that the vapour of water in the air is not raised to nearly the temperature of melting platinum by any action which takes place in the growth of plants. This other law is, again, comparable to evaporation; for although water boils, or is wholly converted into vapour, at

212 degs., it evaporates, or is partially converted into vapour, at very much lower temperatures—at all temperatures, in fact, for even ice and snow evaporate slowly. Dissociation of water, in like manner, occurs in small degrees, even at comparatively moderate temperatures. Deville showed this experimentally, and proved that the analogy to evaporation is here strictly maintained, but under ordinary circumstances the elements of the water recombine. The complete dissociation-temperature, like the boiling-point, is lowered as the pressure of the air is diminished.

To effect the reduction of the noble metals—platinum, gold, and silver, for example—we have nothing to do but simply to raise their temperature; their affinities for oxygen or sulphur are so weak that a moderate heat dissociates them at once. Mercury, as already explained, stands between the noble and the plebeian metals. Its oxygen may be driven off by a certain degree of heat, and may be brought back again by another. It is, however, usually classed with the noble metals. In the practical reduction of its ores it is treated both as a noble and as a plebeian metal; by one process heat only is applied, by others this is aided by other chemical agency.

Lower down in the plebeian direction are such metals as tin, lead, and copper. The oxides and sulphides of these are not reducible by mere heating; but if they are suitably mixed with charcoal, and then heated, the metal is separated readily. In practical metallurgy, this separation is not effected quite so simply, because the ordinary ores are not pure sulphides or pure oxides. The other impurities have to be removed, as well as the sulphur and oxygen; and in some cases they have to be prevented from forming troublesome compounds with the oxides. Thus, in the smelting of tin ore special precautions are necessary in order to

prevent the oxide from combining with the silica in the ore, and forming masses of enamel, the separation of the metal from which is more difficult than from the original ore.

Iron is still lower than these—*i.e.*, its affinity for oxygen is still stronger, and the temperature demanded for its dissociation from oxygen is still higher—so high, in fact, that by heat alone the reduction of iron ores is *practically* impossible. Here the great reducing auxiliary is carbon. Cold carbon and cold iron oxide, lying side by side, or however intimately mixed, have no visible action on each other, though to say that there is no absolute action would be venturing too far; but in practical work we may regard them as inert.

When carbon in the form of charcoal, coke, &c., is heated, it acquires, as the temperature rises, a continually-increasing affinity for oxygen, until at last this becomes manifest in ordinary combustion.

We make a mistake, however, if we conclude that coal only burns when it smokes, glows, or blazes. It may, and often does, burn very quietly. If a thermometer be placed in a heap of coal-slack that has long been standing, it will be found to indicate a temperature above that of the outer air. I once suffered a costly experience of this. I had contracted for a supply of cannel-slack, to be distilled for its liquid hydro-carbons. The delivery was made more rapidly than the retorts could work it off, and large heaps were accordingly stacked by the siding, and worked from their surface—*i.e.*, the newest first. After a while, the product declined, grew worse and worse, and finally the slack proved to be a sort of semi-coke, that did not yield enough to pay for the cost of distillation. This was due to slow combustion, or what is popularly called 'spontaneous combustion.'

But, returning to the action between the oxide of iron and the carbon, we have, on heating them together, two concurrent actions tending to the separation of the oxygen and reduction of the iron. The heat starts its work of dissociation of the compound by counteracting or weakening the affinities or chemical attractions of its constituents, doing this more and more effectively as the temperature rises; and, at the same time, this rise of temperature increases the thirst of the carbon for oxygen, until at last the oxygen, pushed from the iron by the one force, and pulled from it by the other, leaves it altogether, and combines with the carbon, to form its gaseous carbon compounds; and thus the reduction is effected.

There appears to be a contradiction here, and there certainly is a difficulty sufficient to check any too sweeping generalisations concerning the merely repulsive or separative action of heat. Its effect on the carbon is to aid combination, instead of effecting dissociation. This is puzzling, but it very commonly occurs. The case of mercury combining at one temperature with oxygen, as already described, and then throwing it off at a higher temperature, is in point; and, as we all know, iron becomes rapidly oxidised at a red heat.

In further illustration of these operations of dissociation and reduction, I will take the case of the manufacture of iron by the primitive ironmasters, who used only the black, or magnetic oxide as their ore, and wood charcoal as their fuel and reducing agent. The rationale of the changes will thus be presented without the complications which occur in our modern blast furnaces—complications which, as will be seen hereafter, are due to interfering impurities both of ore and fuel.

In the simple treatment of oxide of iron with charcoal,

the carbon of the charcoal assists the dissociation of the iron oxide by its own affinity for oxygen, and by offering to it a gas that also greedily combines with oxygen—viz., carbonic oxide, which is the gas formed in the first step of the combustion of the charcoal. It is composed of one equivalent of carbon and one of oxygen (CO), and burns with a blue flame when heated in the air, thereby forming carbonic acid, otherwise named 'carbonic dioxide' (CO_2).

When in the midst of the fire, surrounded by the unburnt charcoal, carbonic oxide cannot thus combine with the oxygen of the air, and remain as carbonic acid, for carbonic acid itself is dissociated by contact with red-hot charcoal, and thereby separated into carbonic oxide and precipitated carbon. Carbonic oxide, therefore, acts upon the iron ore just when the oxide reaches that temperature at which its oxygen is nearly separated by the dissociating action of the heat, and thus metallic iron is separated.

At the moment of this separation the oxide is in a semi-fused, or pasty condition, and the gas issuing from this boils it up into a sort of froth. At the same time something else occurs. The iron thus separated is less fusible than the oxide, and therefore the froth, as it loses its oxygen, partially solidifies, and becomes a sponge composed of semi-solid iron, not sufficiently fluid to run down as a liquid, and form a metallic button, but soft and pasty enough to be compressible into a solid mass—*i.e.*, weldable.

In this state it needs only to be squeezed or hammered in order to become compact metal. Both the ancient and modern ironmakers have availed themselves of this condition of the iron-sponge to form it into balls, or blooms of malleable iron.

The primitive ironmasters did this by simply picking out the iron-sponge from the midst of their simple furnaces,

and then beating together the small balls, or blooms thus obtained. Their various methods of working, the forms of their furnaces, and the devices for obtaining a blast, however interesting, do not come within my present province, which is the rationale, not the machinery, of iron-making.

One important fact in reference to the requirement for such machinery should, however, be named, as it greatly simplifies all the necessary devices—this is, that charcoal itself is so light, and the small quantity of ash it leaves after combustion is such flimsy, flocculent material, that the iron-sponge settles down spontaneously amongst it, and may all be gathered into one manageable bloom, by a very small amount of poking or coaxing, while in the midst of the hot ashes.

The facility with which this is done may be seen by watching the work of those small modern charcoal-furnaces, or bloomeries, wherein iron scrap is made into charcoal-iron suitable for rolling into wire, or sheets for tin-plating. The scrap and charcoal are put together in a simple fire-box with a blast, and when the whole reaches the full welding-heat, the pieces of scrap stick together and form a bloom, which the workman picks out with his tongs and runs to the hammers. Substitute iron oxide for iron scrap, and ruder materials and tools, and here is a general representation of the ancient bloomeries, and those now worked by the Hindoos, &c.

The second property of iron which assisted the primitive metallurgists, and which still comes largely to the aid of the modern ironmaster, is its readiness, when heated, to unite with carbon and form a series of compounds that fuse at temperatures much lower than that required for the fusion of the pure metal.

The direct action of the carbon in the course of smelting commences as soon as the oxygen of the oxide is reduced, provided there is not an excess of oxygen acting upon it in such wise as to renew the oxidation. Therefore, the weaker the blast, and the more sluggish the furnace, the greater will be the extent of this combination with carbon, or 'cementation.'

This renders it very probable that steel was made quite as early as iron, or even earlier; the first effort of the ancient metallurgist, previously accustomed to the smelting of copper and tin, and the production of bronze by fusion, would be likely to produce, as a final result of tedious efforts with a low-temperature smelting-furnace, some small buttons of melted steel. In repeating this, he would ultimately find the bloom among his ash, and recognise its resemblance to the metal he had obtained by his first method of fusion.

That he should thus produce steel more easily than iron is really less paradoxical than it at first sight appears, seeing that our modern British ironmaster does the same. Pig-iron is really a very impure, excessively carburetted steel; it is obtained as a first-stage product on account of its fusibility rendering its separation from the earthy and other impurities a mere matter of mechanical running down below them. This fusibility is conferred by its combined carbon, and is increased by its silicon, sulphur, and phosphorus impurities, as all these substances, like carbon, form compounds with iron that are far more fusible than the iron itself.

But for these, the process of puddling, and the cementation of bars of iron for the conversion into steel, would never have come into existence, and the old refinery, which is really the primitive form of Bessemer converter

—blowing on the surface instead of below it—would have done all the work of softening the over hard pig-steel by burning out more or less of its carbon, according to the purpose for which the finished product was required.

The reducing agents that practically co-operate with the dissociating agency of heat in separating the oxygen from the ores of iron in practical working are the solid carbon, especially the flocculent deposit produced by the dissociation of carbonic oxide, the carbonic oxide itself, and the hydro-carbon gases.

As we cannot get inside the blast-furnace, and handle these agents, all our statements concerning their efficiency are, necessarily, theoretical and open to question. We have yet much to learn concerning the proceedings that occur within these great fire-towers.

In the following chapters I endeavour to elucidate what is known, or reasonably supposed, without attempting to expound all the theories that have been offered. Such an exposition would certainly be too much for me, and, probably, too much also for my readers.

CHAPTER IV

FLUXING, ROASTING, AND CALCINATION

IN the preceding chapter I explained the chemical philosophy of reduction and dissociation, in order to be able, when treating of the chemistry of the blast furnace, to use the terms freely, and without danger of being misunderstood.

There is another action which is largely involved in the working of the modern blast furnace, and one of absolute necessity and much importance in working inferior ores—*i.e.*, *fluxing*.

This is a most important part of the business of modern iron-making, where the iron oxide is associated with a large quantity of foreign material that must be removed simultaneously with the reduction of the oxide.

I will, therefore, proceed to discuss the chemistry of fluxing, and must do so somewhat at length, as the subject is so widely misunderstood by practical men, and the widespread, popular fallacy, or misunderstanding, to which I refer has remained undisturbed and unrefuted by our teachers of modern science. They must have overlooked the fallacy altogether, or could scarcely have allowed this to be the case, as a very little reflection shows it to be a rather flagrant physical absurdity.

Workmen generally believe that, by adding what is called a flux to a melted or melting metal, the metal

is made to melt at a lower temperature; or that, being melted, the flux renders the metal more fluid.

If this were really the case, it would be a very remarkable fact, well worthy of scientific investigation. It would disturb all our tables of fusing-points and the prevailing scientific doctrines concerning heat-energy and the relations between the solid and liquid states of matter.

Let us first consider the familiar cases of soldering-fluxes. For soft soldering we may use rosin, or ammonium chloride (sal ammoniac), or hydrochloric acid (spirits of salt), or chloride of zinc.

What happens in such cases?

The tinman, for example, places a stick of solder—an alloy of tin and lead—on his work, and applies the soldering-iron. If no flux is used, the solder melted off from the stick forms a little ball, which stands sluggishly on the tin-plate, and is ineffectual. If, on the other hand, a little powdered rosin is there when the soldering-iron is applied, the melted solder 'runs'—spreads itself with decided fluidity over the surface to which the rosin has been applied. The solder flows, and hence the rosin is regarded as a flux.

Take another case. Two pieces of brass, fitted or pressed together with considerable surfaces of contact, are to be united by soldering. If these are placed in the fire simply bound together, and heated to no matter what temperature, and a piece of soft solder be applied at the boundaries of the surfaces in contact, no solder will run between these surfaces. If, however, the surfaces to be soldered were previously moistened by a solution of sal ammoniac, or hydrochloric acid, or chloride of zinc, and more of the solution be dropped or brushed against the edges of the joints just when the metal is at about the heat of boiling water, so that the liquid shall run into the

joints, a great difference is made. The workman now has only to carefully heat the metal to a certain temperature (presently to be defined), when he finds that, on application of the stick of solder, it not only melts, but spreads or runs rapidly over the surface that was moistened by the flux; and if the operation is skilfully performed, it insinuates itself with the fluidity of water between the joints, however close-fitting they may be. The apparent fluidity thus imparted is even more decided than in the first case.

Hard soldering—whether silver soldering or brazing—is performed in a similar manner, excepting that the silver or the 'spelter' (a fusible brass) is applied in granules, mixed with the flux in a state of powder, the flux in these cases being borax.

I have had considerable experience in both hard and soft soldering of brass-work, and after some reflection have framed the following theory:—

I am quite satisfied that these fluxes have no effect on the melting-point of the solder, nor even any direct effect on its fluidity when melted, and believe that their whole efficiency depends on their power of presenting to the melted solder a pure metallic surface to which it can adhere, or, in fact, alloy itself more or less completely.

We know that melted tin, or lead, or zinc, will thus adhere and alloy themselves to clean surfaces of other metals, just as mercury will amalgamate with certain metals. If a piece of dirty brass or copper be dipped into a bath of tin or lead, or the solder-alloy of these, it will come out unaltered; but if it be very carefully cleaned, it will be 'tinned' all over by them. The tinning and galvanising of iron-plates further illustrates this.

How, then, do the above-named fluxes act?

Let us consider the rosin first. This is a hydro-carbon, a powerful reducing agent, which, when heated, combines with the oxygen of such metallic oxides as those of tin, and thus effects a reduction of the pure metal on the surface to which it is applied. Thus, the tinman deoxidises his tin-plate surface, and then his solder amalgamates, or alloys itself freely with it, and runs over, or 'wets' it. I take the liberty of using this term 'wets' on account of its analogy with the familiar action of water, which adheres to some surfaces, or wets them, but runs off of others, such as greasy or dusty surfaces. This difference corresponds to the action of the solder with and without the flux.

But what is the action of the ammonium chloride?

Careful observation enables me to answer this question. After applying the solution, the water dissolving the salt boils off, and there is left behind a white, frost-like coating, of the salt itself. Then we go on applying more heat; and if we are skilful, we watch this white crust, and when we see it begin to dissipate by volatilising in white fumes, we apply the solder before the last of it has gone. Then the solder runs; but if we had applied it sooner, or later, we should have failed.

My explanation is, that the ammoniacal salt dissolves the thin film of oxide, and forms a compound which, like all the other compounds of ammonia, is volatile at a certain temperature. Now, in this case the temperature of volatilisation of the flux corresponds to the melting-point of the solder, and hence their adaptation to each other.

As my practical readers know—especially the old hands—the use of sal ammoniac is now rather old-fashioned, having been nearly superseded by solutions of zinc in hydrochloric acid, or of the acid itself.

The theory I am expounding suggests the reason why the old-fashioned sal ammoniac has been superseded by chloride of zinc. I believe it to be a result of modern adulteration, or rather depreciation, of the solder. Lead being so much cheaper than tin, more and more lead has been added to this alloy. The effect of this is to raise its melting-point, and to demand a flux that shall volatilise at a higher temperature. This demand is supplied by the chloride of zinc. I find, accordingly, that when I make my own solder of two parts tin and one lead—an alloy that fuses at 350 degs. Fahr.—sal ammoniac is a good flux; when I buy the solder ready-made, I succeed better by using chloride of zinc, mixed with free hydrochloric acid.

The action of these is the same as above described: the acid dissolves the oxide on the surface of the work; this solution and the zinc chloride are volatile, as above stated, but at a higher temperature than the ammonia salt.

In my apprentice days, when I received my first lesson in soldering together the segments of a theodolite 'staff-head' before turning it in the lathe, I was told to watch the brass until it became 'beefy,' and then apply the solder.

What was this beefiness?

I have tested this question experimentally, and find that it is due to a removal of a superficial film of zinc from the brass, thus exposing a red, or coppery surface, to which the term 'beefy' may be fairly applied when it is hot and free from oxide. The zinc in the brass oxidises more readily than the copper, the zinc oxide is more readily soluble in hydrochloric acid or chlorides, and zinc oxide and its salts are more volatile than those of copper. Hence the preferential removal of the zinc and the exposure of the beefy copper.

The same beefiness is displayed in hard soldering with

brass or silver, and may be seen, even after the soldering is completed, and the work has cooled, if some portion of the brass surface that was denuded by the flux is not covered by the brass solder. Brass tubes frequently show this on each side of the line of the brazing.

But why is borax used in hard soldering rather than the chlorides; and how does it act?

To answer this question we must consider the chemical properties of borax. It is a compound of boric acid and soda, nearly resembling water-glass, which is a compound of silicic acid and soda. Blowpipe analysis largely consists of fusing metallic oxides with borax, or boric acid, thus obtaining a glass bead, in which the oxide is dissolved, the colour and other appearances of such bead indicating the presence of the particular oxide.

When powdered borax is laid over the metal to be soldered, and the metal is heated, the borax fuses, and forms a glassy film upon the surface of the metal, which film takes up all the oxide, and combines with it, forming a glassy borate of the metal.

But this is not sufficient; for, if that glassy film remained, it would be as bad as the oxide in preventing the adhesion or amalgamation of the solder. Here, then, comes to our aid another property of the borates—viz., their volatility at high temperatures. The borax, with the oxide it has taken up, flies off at a bright-red heat—just at the temperature at which the granules of silver or the spelter-brass melt. Thus, they fuse upon a virgin surface of clean metal, and unite with it.

I have thus gone a little aside from my direct subject, on account of the confusion that the use of this term 'flux' may induce. Borax is also used as a flux in metallurgical operations where a metal, such as gold,

mixed with impurities, is melted. These impurities are taken up by the borax, made into a fusible glass, and thus fluxed or melted away. It is not the gold which is made more fluid, but the oxides of the baser metals that are removed by forming more fusible or volatile compounds when united with the boric acid.

The fluxing in the blast furnace is similar to this. Its action is not the liquefaction of the iron itself, but the gathering together of the impurities of the ore, converting them into a glass that shall fuse and run down with the melted metal; for we must always remember that the fundamental problem of the modern blast furnace is that everything pitched into its throat must come out either as a gas or as a liquid. The retention or formation of any infusible solid would choke, or 'gob' the furnace, and put an end to its profitable operation.

Silicic and boric acid are the two chief glass-making agents, the boric glasses fusing at lower temperatures than the corresponding silicic glasses, and also being more volatile. But we may now dismiss the borates, and confine our attention to the silicates, as they do the fluxing in the blast furnace.

This statement may appear paradoxical for the moment, seeing that not silica, but lime, is the so-called flux of the blast-furnace charge. This is easily explained by reference to the analyses of the clay-ironstone ores already given. They all contain silica, in some cases partly free, as sandy matter, or combined with alumina, or combined with the iron itself.

Silicate of alumina alone is objectionable, on account of its high fusing-point. Silicate of iron fuses readily enough, but is a thief, as it carries away as useless glass the material we are seeking to obtain as reguline metal. We

therefore require to add something that is more powerfully basic than the iron or its oxides, and will therefore combine more readily with the silica; this should form a glass that is readily fusible, and which will, somehow, separate itself from the melted iron. Cheapness is another primary desideratum.

All of these desiderata are united in lime: it is a powerful base, it is very abundant and cheap; its glass is much more fusible than iron, and is so much lighter that it floats freely on the top of the melted iron, and thus may be run off through an overflow conduit or tap-hole. Lime, therefore is used; but it must not be used at random, for the following reasons:

If the supply of lime is not sufficient to combine with the silica, this will unite with the oxide of iron, and form a wasteful iron-glass, or its silicon will remain excessively in combination with the iron itself. If, on the other hand, the lime is in excess, we may get into trouble, due to the fact that uncombined lime is a most refractory substance, is practically infusible, as proved by its use in the limelight, where a mixture of oxygen and hydrogen gases in vivid combustion strikes against a cylinder of lime, making it so intensely white-hot that the light it emits is the most brilliant obtainable. The oxyhydrogen flame is hotter than any furnace yet constructed.

This explanation of the rationale of fluxing in the blast furnace also explains the composition of the *cinder* (so often misnamed 'slag,' as I shall explain hereafter), which carries away everything excepting the pig-iron and the gases. It is mainly a lime-glass, and, being a glass, a multitude of schemes have been devised and patented for using it as a material for bottles, and for other purposes to which glass is applied. The inventors have not sufficiently

considered the fact that lime-glass is much more friable than lead-glass, or soda-glass, or potash-glass, or the mixtures of these that form the material for our windows, bottles, &c.

The problem of utilising this mixture of silicates, in which silicate of lime invariably preponderates, is not yet solved on a scale commensurate with the supply of the material. It still remains a worse than worthless waste product, as its disposal is costly, partly on account of its bulk and weight in carriage, and partly on account of the ground it covers and renders useless. Of all the waste products of British manufactures, this one is about the most unmanageable.

Very pretty, ornamental articles, such as small vases, &c., are now made from it. They resemble onyx, jasper, and agate; but the quantity demanded for such purposes is very trivial compared with the mountains of the material still lying waste.

Looking at these ornaments, and then at the recent revival of the Italian style of internal decoration by marble and *pietra dura* wall-panels, I offer to architects the suggestion that they may obtain exquisite results at moderate cost by availing themselves of this material.

I have described the flux as lime, but should add that, in the practical working of modern furnaces, it is not lime, but limestone, that is mixed with the charge of ore and fuel. Most of my readers know the difference between lime and limestone, but as some may not I will explain it in a few words.

Lime is an oxide of the metal calcium, and this oxide readily combines with carbonic acid, as may be shown by dissolving quicklime in water, or buying a pennyworth of lime-water—which is such a solution—from a druggist, and

then blowing into the clear liquid through a glass tube or the stem of a tobacco-pipe. The liquid presently becomes clouded, and if left at rest a white powder will settle down. This white powder is carbonate of lime, which is insoluble in water, while the quicklime, or oxide of calcium, is soluble.

With care the experiment may be carried further by heating this precipitated powder on a watch-glass, after which it will be found to have regained its solubility. This change presents a simple case of dissociation by heat. The carbonic acid is separated, and flies off as an invisible gas, leaving the caustic (burning) lime behind.

It is this caustic lime, not the carbonate, that combines with the silica, and thereby effects the fluxing by forming fusible lime-glass; therefore, before it can do its work, the lime of the limestone must be dissociated from the carbonic acid.

This may be done in kilns outside the furnace, or in the furnace itself. It is done so easily that the outside apparatus is unnecessary: the upper part of the blast furnace may be its own limekiln, all the limestone of the charge may be calcined or converted into caustic lime, by the heat rising from below.

As already stated, the ores that are most abundant in this country are clay-ironstones, in which the iron exists as carbonate—carbonate of the protoxide, *i.e.*, the lower oxide of iron. Heat dissociates this compound as it dissociates the carbonate of lime: the carbonic acid is separated, expanded into gas, and driven off. Another action accompanies this: the protoxide—a very unstable compound, always thirsting for more oxygen—obtains some more during the roasting, if air is freely admitted, or afterwards, if the protoxide is exposed.

The oxidation that takes place during roasting produces the black, or magnetic oxide, as may be seen by heating a lump of grey ironstone, and observing its change of colour. If this is further exposed to air and water, it reddens superficially, owing to formation of hydrated sesquioxide, or ordinary iron rust.

The oxidation effected in outside roasting is of questionable advantage, as it demands more carbon for its reduction than the original protoxide; but, on the other hand, it is claimed that the higher oxide does not combine with silica to form wasteful iron-glass (Bauermann and others).

I set little value on this claim, having observed that, if silica is heated with any of the higher oxides to the temperature at which it combines with the lower oxide, dissociation of the excess of oxygen takes place, leaving behind the protoxide to combine with the silica.

Another advantage claimed for the outside roasting of iron ores is the decomposition of sulphurets, or iron pyrites (Bauermann and others).

This is questionable, for two reasons: 1st, that scarcely any of the ores which are practically used contain any notable quantity of pyrites; and, 2nd, that, if they did, such roasting would only drive away a portion of the sulphur; would leave behind sufficient to do serious mischief. I discuss this subject more fully when treating the puddling process.

The actual practical advantages of roasting iron ores is limited to the getting rid of water and carbonic acid, and rendering the ironstone more porous. This porosity is decidedly advantageous, as it permits a certain degree of permeation of the gases of the furnace, and thereby exposes a much larger surface of ore to their action. As we shall presently see, these gases are the active reducing agents.

Turning to about the best general technological manual of its date, viz., *Tomlinson's Cyclopædia of Useful Arts* (1854), I find it there stated, that 'Iron ores are not sufficiently valuable to allow of the crushing, stamping, washing, and other processes that precede the reduction of copper, tin, and other ores. They are usually roasted, for the purpose of expelling water and carbonic acid, and producing that porous condition which is favourable to the smelting process. The argillaceous carbonate, or clay-ironstone of the coal-measures, which is the chief source of the iron of this country, and produces from 30 to 33 per cent. of pig-iron, loses by roasting from 25 to 30 parts in every 100. The loss consists chiefly of water and carbonic acid.'

Then follows an account of the 'usual method of roasting the ironstone' in heaps by levelling a piece of ground, covering it with a layer of coal from 6 to 8 inches thick, then arranging upon this 'the pieces of ironstone as nearly the same size as possible' to a height of about 2 feet; of the manner in which this layer is levelled by introducing small pieces of ironstone in the spaces left by the larger pieces; how another layer of small coal of about 2 inches in thickness is cast upon this, and ironstone is then piled up so as to form a wedge-shaped heap, and the whole is lastly covered with small coal, and lighted by applying coals to the ground-stratum at the windward end; and how, after having burned to a certain distance, the pile is prolonged in the opposite direction, the fire creeping along, gradually igniting the whole heap from top to bottom; and how, 'when the coals are all burnt out, the pile gradually cools, and in about a month from the commencement of the operation the ore is fit for the furnace.'

Here, as in other and larger and later treatises, roasting-kilns of various construction are also described. In like manner, we find chapters devoted to coke heaps and coke-ovens, and also to the kilns used for the preparatory roasting of the limestone flux, whereby the carbonic acid is driven off, and caustic lime remains.

If, however, we continue moving in the present line of progress, all these will, ere long, have only an historical interest, for a reason that is sufficiently evident. Imagine a blast furnace of, say, 50 feet in height, and by its side the roasting-kilns for the ores, the coke-ovens, and the limekilns. These may either be fed by their own special supplies of coal, or may be heated by the waste gases of the blast furnace, carried down to them by expensive apparatus. In either of these cases the furnace will be charged with roasted ore, coke, and quicklime.

Now let us suppose that we build this furnace 10 or a dozen feet higher, and that its work shall otherwise be the same up to the original 50 feet. What will happen if we charge it with raw ore, raw coal, and raw limestone, filling up the additional 10 or 12 feet with these? We shall obviously have the original furnace surmounted by a roasting-kiln, a coke-oven, and limekiln all in one, and the triple work of these done by the waste heat of the furnace in the simplest conceivable manner.

This is actually done, more or less completely, in our modern and very tall blast furnaces, which have reached to 100 feet in height. It is not quite so easily done in practice as in the above imaginary sketch, because the additional burden presses on the material below, and impedes, more or less, the outward passage of the gases formed below; besides this, one of our imaginary conditions (imagined for simplicity of exposition) cannot be

fully carried out—viz., that of piling the charge 10 or 12 feet higher, and leaving the condition below the same as before, height for height. With this addition, the temperature at the original limit of the furnace—the 50 feet of height—will be higher than when this was the exposed surface, and the condition of all below is sympathetically affected.

As already stated, the working of a blast furnace is a delicate operation. The various conditions of dimensions, force and temperature of blast, proportions of charge, &c., have been discovered by experience, and any large alteration of any one of these, without compensating adjustment of the rest, is dangerous, and may produce very costly disaster; therefore, the increase of height and the change from prepared to raw materials, can scarcely be made at a bound, but must be done step by step, feeling the way all the while, for we still are so much in the dark, theoretically, that we must work by the old, empirical method of watching results rather than under the guidance of any brilliant theoretical anticipations. The records of our Patent Office, and the ruinous efforts of so many ingenious inventors, afford melancholy evidence of this.

Nevertheless, I have no hesitation in affirming that any blast furnace which does not roast its own ores, coke all its own coal, and alkalise its own lime, is an imperfect machine, with which the enterprising ironmaster should continue to be dissatisfied, and should continually seek to improve until it does this without any accompanying disadvantage. Here is a clearly-definable theoretical and reasonable demand, which practical skill is bound to satisfy.

It may be replied to this, that 'we cannot eat our cake and have it'; that, if we use the residual heat that comes

up from below for the purposes named, we shall have so much less remaining to be carried by the modern appliances to the blast-heating and boiler-furnaces. This is quite true as regards the calcination of the ore and the lime. Both of these operations of separating and expanding carbonic acid and water are attended with a considerable loss of heat.

But in the coking of the coal there is a compensation, for this operation is chiefly a distillation, or driving off, of combustible gases—the same as in the retorts of the gasworks; these hydro-carbon gases are thereby added to the carbonic oxide, and thus supply so much more gaseous fuel which, by suitable means, can be carried away unburnt, and then lighted just where its heat of combustion is required. In ordinary coke heaps and coke-ovens these gases are wasted. This, if I mistake not, more than compensates for the whole loss in the calcination of the ore and limestone.

There is, however, one case where practice and theory come in apparent collision, and where it may be cheaper to roast the ores and limestone outside the blast furnace, with outside fuel, than to do so by increasing the height of the furnace and making the other concomitant modifications.

This is where coal-slack is so abundant and cheap that it practically costs almost nothing. I have seen it used as ballast for railways in North Wales, simply because it was unsaleable on the spot at 18*d.* per ton, and the carriage of gravel to the colliery-siding where the stack stood and the ballast was wanted cost more than 18*d.* per ton. Improvements in the manufacture of what has been called 'artificial fuel'—*i.e.*, compressed or otherwise consolidated slack—will put an end to this condition.

Increased price of coal and improvements in getting it will act in the same direction. But in all these yearnings for theoretical perfection we must keep in view the practical surroundings, especially in reference to fuel economy.

A great deal of nonsense has been written and spoken on this subject by very learned men, who, in spite of their science, were ignorant of the fact that economy of fuel may be very costly where labour is dear and fuel abundant: that the colliery proprietor who gets his coal at 4*s*. per ton and his labour at 5*s*. per day is reasonably deaf and blind to scientific demonstration which shows how he may save a ton of coals at the cost of a day's labour, or a corresponding outlay of capital.

CHAPTER V

THE BLAST FURNACE

Descent of the Charge

I ASSUME that my readers are sufficiently acquainted with the ordinary forms of the blast furnace to render unnecessary any minute description of mechanical details. Speaking generally, it is a tall, hollow tower of masonry, braced with iron and lined with fire-brick. Having been duly started, or 'blown in,' and thereby filled with a burning mass of fuel, ore, and flux, its charge is maintained by adding fresh fuel, ore, and flux from time to time, or continuously, at the top, and the fused metal and cinder are tapped out from the bottom.

A little reflection on this simple general statement of primary conditions suggests a problem we usually overlook when examining the details of the construction and action of the blast furnace. It is this:

What becomes of the incombustible ash of the coal?

There is no raking out of fire-bars, no ashpit, or other means of disposing of any sort of solid refuse, either from the ore or the coal. Nothing but liquid can find its way out of this furnace. As we all know, this problem is practically solved when a furnace is working properly.

It is obvious at a glance that success or failure in this respect must depend upon the chemical composition of

the whole of the charge; for, as some compounds are fusible, and others are not, the charge, as a whole, must be so composed and proportioned that it shall, when heated, so combine as to form only a fusible result. Inventors who are bent upon making improvements in blast furnaces are rather apt to overlook this primary necessity, and omit to consider that the composition of the charges and the methods of working at present adopted are results of long experience, of the teachings of success, and the equally, or even more, valuable teachings of failure; and, therefore, that any interference with them is attended with considerable risk.

This explains the fact that ironmasters who so liberally allow investigators and inventors to make experiments in their puddling-furnaces, &c., are not so ready to permit interferences with the working of their blast furnaces.

The reader will learn from these considerations that the rationale of the charge of the blast furnace is not so simple as it might have at first sight appeared. There is much to be provided for: First, we have to remove the heterogeneous impurities from the very complex clay-ironstone ores; secondly, we have to reduce the iron they contain to the reguline, or metallic, state; thirdly, we have to make this iron fusible; and, fourthly, we have to render fusible all the earthy impurities we have removed from the ore, and also those which are left behind in the incombustible ash of the coal. All this must so proceed that, when the charge reaches the bottom of the furnace, all shall become liquid *just then, and not before*; so that up to this moment they shall bear the burden of the mass above them, and *at* this moment all that remains of them shall run down into the crucible or receptacle provided to receive them in their liquid state.

With the composition of the various ores before us, and a definite statement of the conditions of the problem of modern iron-smelting, we are now prepared to follow rationally the actions which occur in our blast furnaces. The problem is not an easy one, on account of the absolute invisibility of the whole proceeding. Not only are the doings within these great fire-towers veiled from our eyes by the wall of brickwork, but our attempts to extort their secrets by indirect, experimental prying are more or less frustrated by the high temperatures that prevail. Samples have been drawn from various parts of the furnace; and from these, as we shall see, valuable information is obtainable: but even these tell us but little, unless we interpret their appearance by a knowledge, otherwise obtained, of possible and probable chemical reactions.

Although it is not necessary to describe all the mechanical details of the blast furnace or other machinery of iron-making in order to discuss the chemistry of the actions proceeding therein, there are some features in the construction of the blast furnace which, although merely mechanical in themselves, are fundamentally connected with the philosophy of iron-smelting. This may be supposed *à priori*, when we consider that the existing forms and dimensions of blast furnaces are the result of accumulated experience; and although 'the rule-of-thumb' may have been the chief guide in determining these features of construction, there must be, underlying such empirical rules, some natural principle or principles upon which the thumb-rule, if correct, must of necessity be based, however ignorant its followers may have been of such principles.

There is a great deal more of unacknowledged science in the proceedings of workmen than pure scientists are inclined to admit or able to perceive.

One of the most remarkable features of the modern blast furnace, as compared with those of earlier date, is its great height. The ancient bloomeries, and the blast furnaces of the present-day primitive ironworkers—those of India, Burmah, China, Borneo, Africa, &c.—as well as the Corsican, or Catalan furnace, still used in the neighbourhood of the Pyrenees and other parts of South Europe, are all of very small height—not merely low on account of the smallness of the charge, but very low even in proportion to this. Their height, in fact, but slightly exceeds their breadth. There must be some reason for this long-persisting difference. What is it?

These furnaces were, and are, only used for the reduction of the richest and purest ores by means of nearly pure carbon—*i.e.*, wood-charcoal.

For illustration sake I will take the Catalan, or Corsican furnace, which is fairly typical of the class in question. The hearth of this furnace is hollowed, or basin-shaped, with a perpendicular wall on the side, through which the blast enters, and a convex wall rounding away on the other side. This convex wall, being roofed over by a concave continuation of the opposite perpendicular wall, forms the beginning of the chimney-shaft. The bottom of the hearth is of refractory sandstone, lined with a coating of charcoal dust. The charge of ore is piled on the hearth, and heaped over the curved wall opposite the tuyere, lying evenly or parallel to the curved wall, which thus forms a sort of supplementary or reserve hearth.

The hearth proper is filled up with charcoal enveloping the heap of ore, and this, again, is covered over with *greillade—i.e.*, the small ore and charcoal dust moistened and matted together. A gentle blast is at first applied, and when the flame bursts through the greillade more is

laid over it, to damp the combustion and prevent the reserve heap on the curved wall from coming down too soon. This is continued for about two hours; then the blast is turned on fully, and the fluid cinder is tapped out. The ore lying on the curved wall is now pushed gradually down. Having been exposed to the flame and heated products of combustion from the lower part, it is already in condition to receive the full blast, and thus contribute at once to the result. The blast is continued until the whole of both the primary and reserve charge is reduced, and a mass of spongy iron is formed, which rests on the bottom hearth, below the fused cinder. This spongy iron is brought out in a pasty, solid state, and corresponds, not to the pig-iron product of our blast furnaces, but to the ball which is brought out of the puddling-furnace.

The puddling process is entirely superseded in these simple blast furnaces; and at first sight it appears rather contradictory that the work which, with improved appliances, demands two large, elaborated furnaces, should be done by a primitive, small, and simple one. This apparent contradiction arises, primarily, from the difference of the quality of material used, and, further, from the differences of quantity in operation. The material used in the Catalan furnace is usually hematite; in the still more primitive furnaces, it is magnetic oxide. In either case, very little beyond mere reduction is required. Besides this, the fuel being nearly pure carbon, effects the reduction without doing other work to which our coal or coke is addicted.

Recent experiments have shown that the reduction of the oxide of iron contained in iron ores, and the production of spongy iron therefrom, takes place at a lower temperature than was formerly supposed.

According to Mr. Lowthian Bell, it occurs in our modern

blast furnaces quite near to the top, where the descending charge has only just attained a dull red heat, and where the coal is but just fully coked. This 'zone of reduction,' as Mr. Bell calls it, which extends only down to about one-fifth of the distance between the throat of the furnace and the crucible, corresponds in its action to the Catalan furnace. Above it is the reserve of ore, &c., corresponding to the reserve on the curved wall. This is being roasted or calcined, and heated in preparation for reduction, and then it descends fairly into the zone of reduction, corresponding nearly, but not fully, to the bottom hollow of the Catalan furnace. There is spongy and completely reduced metal in both. This has been proved by withdrawing samples from openings made for the purpose in the side of the furnaces.

But why not stop here? is the question usually asked when this is explained.

The answer to this question is of no small practical importance, seeing that many thousands of pounds have been expended, many patents secured and abandoned, all having this object in view—the production of malleable iron directly from the ore.

It is not at all surprising that such should have been the case, seeing that the experiments that have been made by withdrawing specimens of the iron-sponge from the upper part of a blast furnace and then melting them have shown that the iron is far less impure than the pig-iron, or final product of ordinary working. Nearly all the sulphur which exists in pig-iron is obtained from the fuel in the course of its subsequent downward progress in the blast furnace.

The seductive theoretical simplicity of the idea of direct production of iron is well stated in the following extract

from a paper read before the American Institute of Mining Engineers, February 1874, by Mr. Thomas S. Blair, of Pittsburgh, who has struggled very heroically with this problem.

He says, 'We take a small porcelain tube and fill it with a mixture of pulverised peroxide of iron and charcoal; next we seal the ends of the tube hermetically, then expose it to heat by immersing it in a bath of brightly red-hot sand for a certain time (varying with the character of the ore), then take it out, cool it, and, after cooling, break it open and pour out the contents. Carefully separating and testing them, we find we have obtained particles of metallic iron. Now, what conditions did we observe to get this result? (1) There was contact of the iron oxide with carbon. (2) There was isolation from the free oxygen of the atmosphere. (3) There was the heat of bright redness. (4) There was a certain duration of time. (5) There was a continued isolation from the air until cold. Hence we have established the fact that if a peroxide of iron be brought into contact with a sufficient quantity of carbon, with perfect isolation from the atmosphere, while exposed for a sufficient length of time to a sufficient heat, and then cooled down to a sufficient degree while still isolated from the air, the oxygen and the iron will be dissociated, the oxygen passing off in the gaseous form, leaving the iron behind. Now, chemistry supplies all the data for filling up with absolute figures the blanks in this statement, and we have in consequence a formula by which, if strictly carried out, we can achieve the first of our two great steps in the direct process; we can gain the metallic iron direct from the ore. Hence the chemistry of the operation is clear, and it becomes simply an engineering question how to meet all the necessary conditions, so as to conduct it on a large scale.'

Others have reasoned in the same manner both before and since this address was read, and have been most sanguine of success. Chenot, for example, received from the jury of the French Exposition of 1855 one of the great gold medals for supposed success; and Le Play describes Chenot's process as 'the greatest metallurgical discovery of the age.'

It would carry me too far aside to describe only a few of the multitude of efforts all directed to this end, the various forms of retorts, reducing chambers, cooling or quenching devices, magnetic separators of the pulverised sponge, &c., &c.; but I will go a little further into the details of Blair's process, as it directly aims at imitating a blast furnace so far down as to the zone of reduction, and then stopping at that stage.

I visited the works that were erected in this country on a practical scale a few years ago by the Blair Iron and Steel Company. Their operations were very interesting and instructive. The general furnace was a cylindrical brick tower 42 feet high and between 5 and 6 feet diameter outside; the internal diameter being 4½ feet. As in the blast furnace, to which it thus bore a certain degree of external resemblance, the charge is thrown in at the top of the tower and the metal withdrawn from the bottom. The space to receive the charge was an annular chamber. This was formed by the insertion at the top of the tower of what Mr. Blair called 'a thimble,' an inner hollow cylinder closed at the bottom, and of depth equal to about one-sixth of the height of the tower. Its diameter was 32 inches, thus giving 5 inches as the thickness of the annular space into which the mixture of ore and carbon without flux was charged. This annular space corresponded in position and depth to the 'zone of

reduction' of an ordinary blast furnace, and its temperature was maintained at the necessary heat for reduction only, by surrounding the upper part of the cylinder with a brick jacket, between which and the cylinder was an annular space. This space was heated by crude gas produced in a suitable generator, sight holes being provided for observing the depth of glow. The interior of the thimble was heated by means of the carbonic oxide produced by the reduction of the ore, which, together with air for its combustion, was introduced by suitable pipes.

Thus an annulus of ore and carbon, 5 inches thick, 6 or 7 feet deep, and 4½ feet external diameter, was heated from both sides. After the charge has passed the thimble in the course of its descent, it spreads under it and fills the whole of the hollow tower, remaining at the reducing heat for some distance, and then gradually cooling; the final cooling being accelerated by a water jacket which surrounds the lower part. The sponge is finally discharged at the bottom, and has to be melted in order to separate the impurities of the ore, which are, of course, entangled in the sponge. These float away as cinder, and to effect this separation a flux may or may not be required, according to the nature of the impurities.

One of the instructive results of the working of this process was a practical confirmation of Mr. Lowthian Bell's statement that the intensity of the action of reduction is by no means proportionate to the degree of heat employed. Once the temperature of reduction is obtained, nothing is gained, so far as reduction is concerned, by raising it any higher. Even the speed of action indicates no particular acceleration by such increase of heat.

Mr. Blair further states that he finds that at the true

temperature of reduction no carbon is taken up by the iron, however great may be the excess of carbon used, but that a higher temperature must be obtained before cementation commences. This is not in accordance with what is generally understood, nor with ordinary experience in casehardening. It is generally supposed that by long 'soaking' with carbon, even at a low red heat, iron may be converted into steel.

Why, then, have this and other direct processes failed when thus conducted on a practically large scale?

My object in describing Blair's process—the most hopeful of all the attempts at direct iron-making—is to bring out this question and its answer, which show in broad relief the advantages of the blast furnace. The chief reasons why it has not superseded our existing blast furnaces are: (1) that it demands very rich ores in the reducing furnaces, or otherwise a great expenditure of fuel; (2) that, simple and direct as it appears, the necessity for the melting of the sponge involves a greater cost than puddling. It must either be melted in pots with spiegeleisen, or other similar carburetted iron, to form steel, as was done when I saw the process in operation, or in a Siemens-Martin, or other equivalent furnace, as was done at Glenwood in the United States. The fusion of the spongy iron, as iron, without conversion into steel, is even more costly than converting it into steel, on account of the high fusing point of such iron and its liability to oxidise.

The modern blast furnace, as already stated, is a hollow fire-tower varying in height from about 30 to 100 feet, constructed of substantial masonry braced with iron and lined with a 'shirt' of refractory material such as fire-brick. The shape of the outside need not be considered

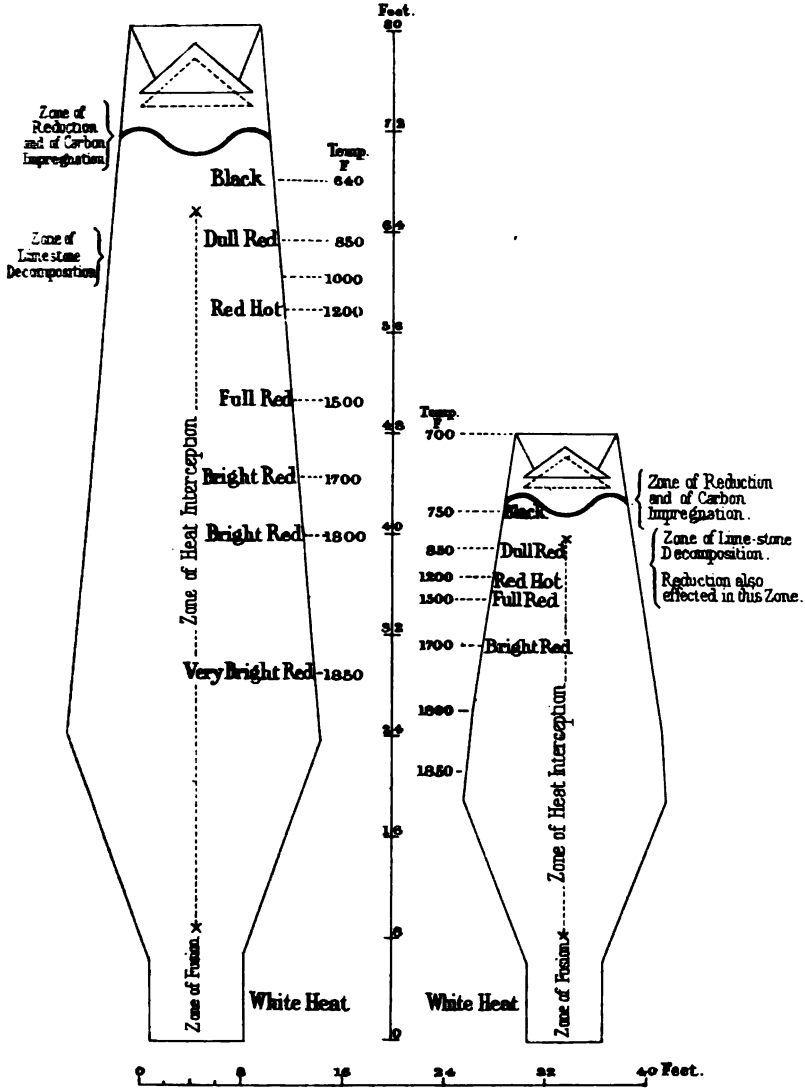
here as it is determined by mechanical and architectural considerations, but that of the inside has considerable chemical significance. The modern form is shown in the annexed diagrams of vertical sections of the interior of two furnaces of different heights and capacities, for which diagrams I am indebted to Mr. Lowthian Bell, whose description of their shape is happily concise, viz. 'a circular column swelling in diameter from both extremities.' It will be observed that the lowest part is cylindrical in the diagram, but this is not necessarily the case. It is merely the receptacle for the fused results and may be thus shaped, or (as in some of the Shropshire furnaces) it may be a continuation of the lower inverted cone.

In describing the action of the different parts of the furnace, it will save circumlocution if I use a few technical terms, those generally accepted.

The topmost portion, which in older forms of furnaces is cylindrical, is well named the '*throat*,' as down it is poured the charge. In the older furnace this is surmounted by the *tunnel head*, which is merely a short chimney on the top of which the waste gases burn in the air, the side being tunneled to form an opening for charging and protecting the charger from this flame.

In the diagram the more modern device of *cup and cone* occupies the throat, which is closed by the cone (shown in section as a triangle) excepting at the moment when the charge is dropped from the cup by lowering the cone to the position shown by the dotted lines. I need scarcely add that the object of this is to allow the waste gases to be carried away by a suitable tube—not shown—and utilised for heating the blast, &c.

All that portion of the furnace extending downwards from the throat to the widest part is called the *stack*.


Feet.
Temp. F
Zone of Reduction and of Carbon Impregnation.
Zone of Lime-stone Decomposition.
Black
Dull Red
Red Hot
Full Red
Bright Red
Bright Red
Very Bright Red
840
850
1000
1200
1500
1700
1800
1850
Zone of Heat Interception.
Zone of Fusion.
White Heat
Temp. F
700
750
850
1200
1500
1700
1800
1850
Black
Dull Red
Red Hot
Full Red
Bright Red
Zone of Reduction and of Carbon Impregnation.
Zone of Lime-stone Decomposition.
Reduction also effected in this Zone.
Zone of Heat Interception.
Zone of Fusion.
White Heat
0
8
16
24
32
40 Feet.

Its greatest expansion where it curves into the contracting portion below, is called the *bosh* or *boshes*—a word which Bauerman and others tell us is possibly a corruption of the German *bauch*, belly. I question this. Our mining and metallurgical predecessors were not the Germans but the Scandinavians. I think it far more likely that the parent word is *bossel*, the Scandinavian for bowl, especially as in the old and some modern furnaces this part was decidedly bowl-shaped.

The bottom portion, or receptacle for the liquid results, is the *crucible*, also called the *hearth*.

The temperatures stated on the diagrams are those which have been determined experimentally by Mr. Lowthian Bell.

The gradual reduction of temperature upwards presents an apparent contradiction of the popular dictum that heat ascends, but is not quite as it appears, for here the heat decidedly ascends, seeing that the materials charged into the top are cold, and the gases that come out there have a temperature a little above the melting-point of lead.

The true reason for the differences of temperature is simple enough; the heat in the furnace being caused by the combustion of the fuel, it is greatest where the greatest quantity and intensity of combustion occurs, and this, of course, is just at the place where it receives the fresh oxygen of the blast, viz., near the mouths of the tuyeres, or blast tubes which enter just above the melted metal in the crucible.

If these were placed at the middle or the top, the greatest heat would be there, irrespective of ascent or descent. The cooling that occurs upwards is due, first, to the fact that, although the supply of fresh unburnt fuel

increases with the ascent, that of fresh uncombined oxygen diminishes; and secondly, because the heat generated below has work to do on its way upwards.

In the first place it has to communicate itself to a continually increasing bulk of material as it ascends from the crucible to the boshes. Secondly, and more exhaustively, it has to do much dissociation work, and the work of expanding solids into gases. It must never be forgotten that heat-power is as necessarily exhausted in doing such work, as mechanical power is in driving machinery.

There are two ways of following the work done in a blast furnace: we may travel in imagination downwards with the charge, or upwards with the blast. After some hesitation and reflection in determining which to choose, I have decided to take both—the descending course as regards the result of the action, and the ascending course for the explanation of the causes of these results. The facts in the descending course may be treated briefly and generally, but the theory which I shall have to expound in working upwards will require more lengthened discussion.

We start, then, from the top with a charge of ironstone and coal, or coke, or a mixture of coal and coke, and with limestone or lime. Let us suppose that the limestone is uncalcined, the ore is raw, and that a considerable proportion of raw coal is used.

At the temperature of the throat, between 600 deg. and 700 deg. Fahr. in a tall furnace, the distillation of the raw coal commences; its water, and with it some of its ammonia is driven off. The roasting of the raw ore also commences with the driving off of its adhering and chemically-combined water; the latter effecting the dehydration of the hydrated oxides.

Lower down, as the black heat approaches to the dull red, the bituminous matter of the coal comes off as tar and naphtha vapours, and the roasting of the ore is completed.

Here, also, the reduction commences, or, according to Mr. Lowthian Bell, even before this, but this doubtless depends on the nature of the ore. A loose hematite is more easily reduced than a compact raw carbonate, and its reduction commences at a lower temperature, both on account of its structure, and because it is quite ready for reduction; but the carbonate is not so. It must first become roasted, *i.e.*, its carbonic acid must be driven off; this driving off of carbonic acid exhausts the heat-power, keeps down the actual temperature of the ore itself below that of its surroundings, and also lowers the temperature of the ascending gases that are in immediate contact with it.

Besides this, the actual particles of iron oxide are more or less surrounded and defended by the silicates, the alumina, and general impurities of the lower classes of ores. These confer a refractory character on the ore demanding a higher temperature for reduction. I have little doubt that one of the reasons why the Cleveland furnaces are so exceptionally tall is that there is more work demanded of them in their upper regions on account of the impurity, poverty, and obstinacy of the Cleveland ores.

Just about the temperature at which the driving-off of the carbonic acid from the ironstone is completed, the corresponding decomposition of the limestone commences, for carbonic acid holds to lime with a firmer chemical grip than to iron oxide, and accordingly requires a higher temperature to effect its dissociation by the unaided repulsive action of the heat. When a full red heat is attained all the iron oxide is reduced to the state of spongy iron, and

all the limestone is decomposed to quicklime, the coal having been completely coked already.

Here, then, commences the speciality of the modern blast furnace. It was here, as already described, that the Catalan and other old processes of direct malleable iron-making finished; here or hereabouts they drew their blooms and hammered the spongy iron into bars, or by further exposure to their charcoal fires converted it into fusible steel. But as our diagram shows, the charge is now less than half-way down the modern furnace.

As it proceeds the particles of reduced iron in the sponge, though pure enough in their small selves, get into bad company; they associate with the phosphorus that has been reduced from the phosphoric acid of the organic matter in the ore; they unite in like manner with the sulphur that has been separated from the pyrites of the coal; and they also combine with the carbon of the fuel in a manner which will require explanation when we make our theoretical upward journey.

Besides this, they take up the silicon which is now becoming dissociated from the silicic acid of the earthy siliceous impurities of the ores, and thus we have phosphide, sulphide, carbide, and silicide of iron, the proportions of which to the original uncombined iron go on increasing as the charge proceeds downwards to the boshes, and the furnace begins to narrow.

What then?

All these compounds differ from pure iron in their far greater degree of fusibility. They are not only more fusible than the iron itself, but when fused they have the power of dissolving the less fusible iron in a manner analogous to the solution of sugar and saline substances in water; or, to take a nearer analogy, to resinous substances

in turpentine or other essential oil, *i.e.* of solid hydrocarbons in liquid hydrocarbons.

We now reach the rapidly contracting part of the furnace, where the heat becomes more and more concentrated as the tuyeres' mouths are approached. Here accordingly the fusion takes place, and melted metal, with its associated impurities, trickles down amidst the white-hot remains of the solid fuel and finally reaches the crucible.

Another action is going on at the same time. The lime is doing its work by combining with the silica that remains undissociated, or unreduced to silicon. This compound is also fusible; it is a lime glass or silicate of lime. The alumina and other earthy oxides combine with silica and form other glasses, and all these fuse together along with the impure iron; but being of lower specific gravity, they form the fluid cinder (or slag) which floats on the top of the iron, and is run off into the cinder bogies and deposited in the heaps that so questionably decorate our iron-making districts, and still resist our efforts to fully utilise them.

The melted metal goes on accumulating until it fills the crucible, and is then tapped into the larger channels of sand, or 'sows,' the outflow from the sides of which into smaller moulds generates the familiar 'pigs.'

As already stated, the complete fusion of all that enters the furnace and is not driven off as gas is absolutely necessary for its successful working, the characteristic of which is its continuity as compared with the older furnaces, that had to be blown out and blown in again more or less completely. Besides this, it renders the great magnitude of our modern furnaces possible. A little consideration of the effect on the quantity of production and the economy of labour effected by this combination of huge charges

and continuous working shows why we persist in the apparently clumsy paradox of adding impurities that have to be afterwards laboriously eliminated.

Any notable quantity of infusible matter coming down into the narrowing portion of the furnace must stop its action there, or if not there, at the outlet of the cinder, or the tapping hole of the metal. Practice has determined the selection and admixture of ores, the proportions of flux and fuel which secure this essential desideratum, with the greatest economy of material and richness of yield. There are some ores, however, that are especially troublesome by forming infusible 'bears' or 'wolves' on the sides and bottoms of the hearths of the furnaces. The most troublesome of these is made up chiefly of beautiful copper-coloured cubic crystals of what was once supposed to be metallic titanium, but has been shown by Wöhler to be a compound of cyanide with the nitride of titanium. The crystals are individually hard enough to scratch not only glass but agate, and, as I have seen them, are agglomerated in a glassy matrix almost equally hard. The chipping-out of such a bear, when the accumulation is great, is no easy task.

One of the elements of economical working which is connected with the selection of the charge and its fusion, is that of preventing the formation of iron glass by the combination of a portion of the iron in suchwise as to form not merely a silicide, but a silicate, which would run off with the cinder. The old ironworkers wasted a good deal thus, so much that we can now utilise some of their refuse, such as the 'Dane cinders' of the Forest of Dean.

In speaking as above of the 'fusibility' of the material forming the 'fluid' cinder, I used the terms in a practical sense, as indicating that there is sufficient fluidity for the whole to flow out of the furnace.

The fusibility and fluidity are not absolutely complete, inasmuch as a variable amount of infusible material is suspended in the cinder and contributes to its friability, lessening its pure, glassy character and increasing the difficulty of its utilisation for such purposes as those referred to on page 68.

Before closing this chapter, I should say a few words on the difference between 'grey' and 'white' pigs. As all ironworkers know, the grey pigs are granular and soft, while the white pigs are crystalline and excessively hard, harder than ordinary steel.

The primary chemical difference between them is that in the white pig the carbon is combined, as in steel; while in the grey pig most of it is uncombined, *i.e.*, existing separately, and diffused through the mass as grains or scales of graphite or 'plumbago.' In the best No. 1 hematite pig these scales of 'kish' may be picked out with a penknife. In 'mottled' pig there is a mixture of combined and graphitic carbon.

If we dissolve the iron in acid the graphite remains as an insoluble sediment, while the combined carbon remains in the solution, tinging it with a brown colour like that due to a solution of tar. A tarry substance is, in fact, separable from such solution.

So far as I have learned, the difference between these conditions of pig-iron is mainly due to the temperature at which it has been melted, and from which it has been rapidly cooled; the proportion of combined carbon increasing with the heat.

Thus, in the Bessemer converter (see Chapter XV.) the first effect of the blast is to convert the grey iron of the charge into white iron, or the graphitic carbon into combined carbon.

CHAPTER VI

THE BLAST FURNACE

Ascent of the Blast

HAVING followed the charge downwards, from the throat of the blast furnace to the crucible, and noted the principal changes effected in the course of its descent, I now approach the more difficult problem of working theoretically upwards. It may be noted that the changes described in the course of our descending study were chiefly those of the ore and flux; very little notice was taken of what happened to the fuel beyond its coking, its distillation, and its contribution to the impurities of the pig-iron. This important factor must now be treated with far more consideration, and similar attention must be given to the blast. We shall now, in fact, be following the *blast* upwards from its entrance at the tuyeres to its exit at the tunnel head or outlet tube, just as we have already followed the *solid charge* downwards from entrance to exit.

What happens to such a blast of air, carrying with it more or less of aqueous vapour, when projected against a mass of intensely heated carbon?

As everybody knows nowadays, the oxygen of the air acting on ordinary carbon-fuel in ordinary fireplaces produces carbonic acid (CO_2), but the action is not simple and direct. There are two distinct successive operations,

even in this sample case; first the oxygen combines with the solid carbon and forms a gaseous compound, carbonic oxide (CO); this combustible gas then burns by combining with another equivalent of oxygen to form the ultimate result, CO_2.

The simple fact that in open-throat blast furnaces carbonic oxide may be seen in the act of combining with the oxygen of the air—as shown by its characteristic blue flame,—and that we can carry down this combustible gas and use it as fuel, proves that the nett or final result in the blast furnace is incomplete combustion. But even the total absence of the carbonic acid among the gases issuing from the summit of the charge would not prove its absence lower down, or its non-formation at the tuyere region, for carbonic acid is capable of dissociation into carbonic oxide and oxygen by the repulsive separating agency of heat alone. Metallic iron assists this dissociation by taking to itself the second equivalent of oxygen, and carbon acts in like manner.

Whether all the heat which is generated in the region of the blast is produced simply by the conversion of the coke into carbonic oxide, or by this plus the further combustion of more or less of the carbonic oxide and formation of carbonic acid, is a question that has been much discussed. Its solution has been attempted by drawing samples of the gas from different parts of the furnace, and analysing them in order to determine their composition as regards carbonic oxide and carbonic acid. The theoretical results of these trials have been rather contradictory and unsatisfactory in spite of the numerous and careful experiments of Bunsen, Ebelman, Playfair, Rinman, von Tunner, Bell, and others.

As Mr. Lowthian Bell says, 'the opinion commonly received up to a recent period, is that the first action of

the carbon upon the blast converts all the oxygen of the latter into carbonic acid, which gas, meeting on all sides fuel in an intensely heated state, is instantaneously resolved into carbonic oxide. It is difficult to say what has given rise to this view of the method in which oxygen combines with carbon in the blast furnace, for none of the analyses found in works on the subject appear to countenance the explanation formerly adopted. Within two feet of the tuyeres, according to those analyses, the gases contain the carbon almost exclusively as CO, and that it should exist as CO_2 lower down appears to have been inferred rather than proved.'

While I fully agree with the practical conclusion of Mr. Bell that only CO is formed, I think that there is a hitch in his philosophy. He assumes, in common with all his predecessors, that a higher temperature is obtained by the complete combustion of the carbon, *i.e.* its conversion into CO_2, than by its partial combustion or conversion into only CO. He says 'practically, the real question is, does carbon, by its conversion into CO, afford heat of such intensity as to be able to fuse the iron under its influence. If such were not the fact, then the zone of fusion would be confined to that space where a considerable quantity of the carbon exists as carbonic acid, which space is so small that its position has not hitherto been determined.'

My readers will probably be startled by the apparent paradox I am about to enunciate, viz., that a higher temperature is obtainable by the first stage of carbon combustion (the formation of CO only) than is possible where the combustion is completed, and CO_2 is formed; and that this is the case in spite of the fact that more heat is generated in the second case. Or, otherwise stated, my

seeming paradox is, that the partial combustion of carbon, when rapidly effected, produces a higher temperature than is possibly obtainable when its combustion is complete, although more than twice as much heat is evolved by the complete combustion.

This may appear equivalent to asserting that the half is greater than the whole; but a little further explanation will show that it is not so. In the first place, it must be understood that a given quantity of heat may be manifested with greater or less intensity, just as a given quantity of mechanical motion may be effected with greater or less velocity. A given quantity of fuel burning with slow combustion gives out the same quantity of heat as when burning vividly; but, in the first case, the evolution of heat is continued through a proportionately longer time. Thus, the *quantity* of heat produced does not measure its *intensity*, or the height of temperature. Combustion is, simply, chemical combination; ordinary combustion being such combination with the oxygen of the air; the stronger the affinity for oxygen, the more intense the combustion.

In the case under consideration, the primary affinity of the elementary carbon for oxygen is more energetic than the secondary affinity of the compound, CO, for oxygen. The original thirst of the carbon is moderated by its first draught—that producing the CO. Hence we have intense and rapid combustion resulting from the combination of the carbon with the oxygen to form CO, and a further prolonged and milder combustion from the combination of CO with more oxygen to form CO_2.

My view, thus stated, may perhaps appear to be only theoretical; but direct proof is at hand. Deville and his successors have shown that chemical energy is measurable by the heat that is evolved when that energy is exerted as

chemical force by the act of combination, and that the maximum temperature evolved by the combination of any two substances corresponds to that which (under corresponding tension or pressure) is necessary to effect their dissociation by the simple action of heat.

By passing carbonic-acid gas through a tube intensely heated, Deville effected its dissociation into carbonic oxide and oxygen without the aid of any predisposing affinity or precipitation. The dissociation was effected by the repulsive agency of heat alone, at a temperature between 1200 degs. and 1300 degs. Centigrade (= 2192 degs. and 2372 degs. Fahr.). At this temperature, and under the same conditions, the CO was not dissociated, showing that the separation of its elements C and O by simple heating demanded a higher temperature.

In order to grasp the full significance of this, we must remember that, when bodies that would otherwise combine are raised to their dissociation-temperature, their combination is rendered impossible. Deville's experiment shows that simple carbon and simple oxygen can remain together united as carbonic oxide at a temperature and pressure at which carbonic oxide cannot combine with oxygen to form carbonic acid. And therefore, according to the above-named law (that the temperature of dissociation corresponds to that produced by combustion), these experiments show that a more intense heat is generated by the primary combustion of carbon forming CO, than by the secondary combustion of CO forming CO_2.

If this reasoning is correct, we are led to a very important conclusion, of very wide practical application—viz., that whenever coke, or other form of carbon, is in a state of vivid combustion, *the formation of carbonic acid is impossible* in the immediate neighbourhood of the glowing

carbon, for the simple reason that the heat generated by the formation of CO is too intense to allow the combination of the CO with a further dose of oxygen to take place, as no gas can combine when raised to a temperature above its dissociation-point.

This has hitherto been overlooked, and quite a different explanation given to the familiar fact that a brilliantly-glowing carbon fire does not *immediately* produce carbonic acid; for the blue flame commences only at some distance beyond the white-hot, carbon surface. It is described as a consequence of insufficient supply of oxygen; but a little reflection will show that such explanation is quite illogical. It demands a physical impossibility.

The oxygen which produces combustion by its union with the solid carbon comes to it from without. Supposing the supply of oxygen to be limited, and the first action of combination effected—viz., a combination with some of the carbon to form the gaseous CO—the remainder of the carbon will be enveloped in this gas, and thus the next supply of oxygen will encounter the gaseous CO before reaching the solid carbon; and, therefore, if the enveloping gas were as capable of combining with this limited supply of oxygen as the carbon itself, the gas would seize the oxygen before it could reach the solid, as it must pass through the film of CO in order to do so. If this envelope had as energetic an affinity for oxygen (at the temperature of the fire) as that of the simple carbon, it would act as a damper, by using up the supposed insufficient supply before it could reach the solid carbon. But, as we all know, the display of blue flame due to the combustion of carbonic oxide occurs most remarkably when we have a clear, brilliant fire, with most complete combustion; and we see that between the glow-coal and the base of the

blue flames there is a space, evidently occupied by some transparent gas, which, of course, is the carbonic oxide.

My explanation is, that within this space the temperature is above that at which CO can combine with O to form CO_2—or, otherwise stated, is above the temperature of dissociation of carbonic acid; but as soon as the CO gets far enough away from the intensely-heated surface of the coal to cool down below this dissociation-point, then the combustion of CO begins. This leads to some practical conclusions that are quite the opposite of those which follow from the accepted theory.

If I am right, the separate formation, the temporary existence, and possible escape of carbonic oxide, only occurs with abundant supply of air and vivid combustion; for, if the combustion be low and slow, the temperature is favourable for the complete combustion of the carbon and formation of CO_2 at once.

This is verified by facts. No carbonic oxide is traceable in cases of slow combustion, such as that of manure heaps, or in the animal body, neither does it show in slowly-burning stoves; but if we make a common, unlined shop-stove red-hot, there is a noxious escape of carbonic oxide, which passes through the red-hot iron, and diffuses before there is time for its combustion in the air to take place. The headache effect of such ill-constructed stoves is due to this, not to the drying or roasting of the air, as commonly supposed. Carbonic oxide is an active irritant poison. Carbonic acid is merely non-respirable.

In the blast furnace supplied, not only with an abundance of air, but with that blast already heated, we obtain a temperature sufficiently high to prevent the formation of carbonic acid, not merely at the immediate surface of the coke on which the blast is striking, but for

some distance above, through the zone of fusion. This is confirmed by the results of the analyses showing the absence of carbonic acid in this region.

Assuming that the temperatures assigned to the different parts of the blast furnace by Mr. Lowthian Bell are correct, the search for carbonic acid is, demonstrably, a vain one. 1850 degs. Fahr. is the temperature he gives above the boshes; it increases very greatly as we proceed downwards, and therefore must soon reach and exceed 2192 degs., which Deville has shown to be the limit of the possible existence of carbonic acid.

This view being my own, and directly contradicting the generally accepted theory, I have discussed it thus fully, and offer it to my readers for what it is worth.

Whether it be accepted or rejected as a matter of philosophy, we still have the matter of fact that the gas produced by the very intense combustion of carbon in the blast furnace is not CO_2, but is CO. We must remember that this gas is rising through the charge, and that when it reaches the boshes, or thereabouts—*i.e.*, when the sectional area of the contents of the furnace begins to diminish—it has attained a temperature at which it is capable of combining with more oxygen, if it can find any; or, otherwise stated, it there and thereabove becomes an active reducing agent.

So far I have only regarded the blast as diluted oxygen —that is, oxygen diluted with inert nitrogen; but there is another constituent of the atmosphere, and, therefore, also of the blast, which, although small in quantity, is not altogether inactive in the blast furnace.

Careful observers in charge of blast furnaces have noted differences in their working due to differences of weather, especially as between dry and wet weather, and

these are, doubtless, due to the variations in the quantity of aqueous vapour contained in the blast. Systematic and scientific observations and records devoted to this subject would be very interesting, and are still wanting. The record, to be of reliable value, should include more than a comparison between the working on dry and rainy days, because the air may be saturated with vapour without actual rainfall. Absence of rain may thus occur with a considerable range of variation of the proportion of aqueous vapour in the air, so great that, between some days that are ordinarily recorded as dry, and some rainy days, there may be less differences of saturation than between other days that are both described as dry.

But this is not all: the quantity of vapour required to saturate a given quantity of air varies with the temperature, and varies so greatly that, on a dry, summer day, the air usually contains a much larger proportion of aqueous vapour than on a wet day in winter.

According to Leslie, air at 32 degs. Fahr. holds, when saturated, $\frac{1}{160}$ of its own weight of water; at 59 degs., $\frac{1}{80}$; at 86 degs., $\frac{1}{40}$; at 113 degs, $\frac{1}{20}$; and so on. Later experiments indicate a still larger quantity at corresponding temperatures, and a greater rate of increase. Therefore, to make a reliable record of the effect of aqueous vapour in a blast furnace deriving its supply of air in the ordinary manner, a register should be kept of the outside temperature, and also of the hygrometric condition of the atmosphere. Combining these, the real work done by aqueous vapour might be ascertained.

Patents have been secured for supplying the blast artificially with vapour, and the inventors affirm that the iron is improved and the fuel economised thereby; but the experimental researches made by inventors after securing

their patents are peculiar. Unless the patentee is unnaturally strong-minded, his experiments are devoted to demonstrating the advantages of his invention rather than its disadvantages, and are, therefore, necessarily one-sided. We require to know all sides of this question, especially as it appears, in some cases, that an excess of vapour is advantageous, in others objectionable.

But what occurs to the water thus injected with the blast, amounting to about 1 per cent. of the whole material of the blast, on a rough average?

The temperature it attains on reaching the burning coke approaches that at which it becomes dissociated by heat alone; but such dissociation may take place at a much lower temperature if the separating repulsion of heat is aided by chemical attraction of one of its constituents towards an outside substance—an action well and expressively described as a 'predisposing affinity.'

Such predisposing affinity is exerted by the heated coke, which, we know, combines very vigorously with the oxygen of the air blown in by the tuyeres, and therefore must be predisposed to combine in like manner with the oxygen of the aqueous vapour mixed with the air. The uncombined hydrogen which is found to issue from the mouth of the blast furnace confirms this theoretical view.

At first glance it may appear something like theoretical hair-splitting to trace the action of only 1 per cent. of such mere aëriform material as the vapour of water; but this idea vanishes when we test it by figures. A cubic foot of air, compressed by a pressure of 3 lbs. on the square inch—that of an ordinary blast—weighs, in round numbers, 1½ ozs. 10,000 cubic feet of this per minute is but a moderate supply for a modern blast furnace. This weighs

15,000 ozs., 1 per cent. of which is 150 ozs.; 150 ozs. per minute is a little over 562 lbs. per hour. This is a considerable amount of water to be poured upon hot coals, and it must do a proportionate amount of work of some sort.

What is the nature of this work?

In the first place, the act of dissociation is performed at the expense of sensible heat—of an amount just equal to that which is given out in the act of recombination of the hydrogen with the oxygen—*i.e.*, by the combustion in the hydrogen flame. If, in the blast furnace, the dissociation were simply effected by heat alone, a very considerable lowering of temperature would result; but such is not the case. The separation of the oxygen is effected, as above stated, partly by the heat, and partly by the affinity of the incandescent carbon. All this oxygen, when separated, goes to the carbon, combines with it, and thereby gives out a large amount of heat, but not so much as disappeared in dissociating the water.

The researches of Rumford, subsequently confirmed by Favre and Silbermann, show that 8 lbs. of oxygen combining with 1 lb. of hydrogen to form water evolves sufficient heat to raise 34,000 lbs. of water 1 deg. Centigrade; while 8 lbs. of oxygen combining with 24 lbs. of carbon to form carbonic acid evolves only sufficient to raise 23,527 lbs. in the same degree. The difference is apparently due to the heat-work which is demanded for expanding the solid carbon into the gaseous form of carbonic acid, and therefore so much disappears as temperature.

We learn from these facts and figures that, whatever effect aqueous vapour may have, or be supposed to have, on the quality of the iron produced, it certainly does not act as fuel, as many who have accepted the 'water-gas'

theory imagine. On the contrary, it lowers the temperature of the furnace in the degree above stated, and in the same act is consuming fuel. The extent of this consumption of fuel by the dissociated oxygen of the water may be approximately estimated on the basis of the following figures:—

Nine pounds of water contain 8 lbs. of oxygen and 1 lb. of hydrogen. These 8 lbs. of oxygen combine with 6 lbs. of carbon to form carbonic oxide, which is the first result in this region of the furnace. Therefore, the first effect of the 562 lbs. of water per hour, supposing it all to be dissociated, and all its oxygen to combine with the fuel, would be a consumption of eight-ninths of 562 lbs. of fuel, or within a fraction of 500 lbs. per hour; but the carbonic oxide thus formed being a combustible gas, which in modern furnaces is afterwards utilized, the practical final consumption of fuel may be estimated on the basis of the quantity required for the formation of carbonic acid. This is 3 lbs. of carbon to each 9 lbs. of water, giving a total final consumption of carbon fuel by the water amounting to about 154 lbs. per hour.

All this would be dead loss if the separated hydrogen were inert; but such is far from being the case. If in the course of its upward journey the hydrogen could find enough oxygen in the furnace to combine with it, and form water, it would restore all the lost heat by such combustion, minus that which is used in expanding the carbon. This does occur to some extent, but not completely, as proved by the outflow of uncombined hydrogen from the throat of the furnace.

With modern arrangements for utilising these waste gases as fuel for the hot-blast, &c., the final result of the injection of gaseous vapour with the air of the blast is but

small as regards the economy of fuel, when we merely regard the carbon as fuel—*i.e.*, in reference to the amount of heat its combustion evolves. But in the blast furnace the carbon has another function to perform besides heating. It has to act, either directly or indirectly, as the reducing agent that separates the oxygen from the iron in the ore. There are good reasons for concluding that this is done in the blast furnace, not by the solid carbon, but by the gaseous result of its partial oxidation to carbonic oxide.

The water, as we have seen, produces hydrogen when dissociated by the aid of incandescent carbon, and this gas is a reducing agent of even greater power than carbonic oxide. This is easily proved by passing hydrogen over heated oxide of iron; the result is metallic iron and water; the hydrogen is oxidised, the iron oxide deoxidised. Oxides of other metals are similarly reducible.

It must be remembered, however, that whatever reducing work is done by the hydrogen is done very much higher in the furnace than the region of the tuyeres, simply because all the reducing is done before the charge has come so far down. The first action of the aqueous vapour here is, undoubtedly, cooling; but to what extent this loss of heat is compensated by the combustion of the hydrogen on its upward course must depend upon the nature of the charge, the height of the furnace, and other conditions, not so well understood at present as they may be hereafter.

We thus see that carbonic oxide and hydrogen—both reducing agents—are ascending the furnace together, and co-operating to the same effect. This much is fairly certain, but whether they both operate exactly in the same manner on all the constituents of the ore is quite an open question.

We know, for example, that hydrogen combines with phosphorus and sulphur, forming phosphuretted and sulphuretted hydrogen; and it has been assumed by several inventors that it is, therefore, capable of removing these mischievous impurities from the iron, and patents have been secured accordingly. Their abandonment suggests the fallacy of this theory, though it does not absolutely prove it, seeing that the theory of an invention may be sound, and yet it may fail from lack of proper means in carrying it out.

Such records of the effects of water on the blast as above suggested would afford valuable data towards determining the possible purifying agency of hydrogen, especially if exaggerated by the injection of measured quantities of water into the blast pipes, and tested by examining the issuing gases for sulphur and phosphorus, as well as analysing the pigs. Hydrogen, being an element, it cannot possibly do anything in the course of its journey upwards but combine with something that it may meet on the way; it cannot be further dissociated, or leave anything behind, excepting itself, by occlusion in the iron.

This occlusion is a very remarkable action. It is a sort of solution or condensation of the gas within the substance of the metal, bringing the gas to a sort of metallic condition, and forming a compound that has been likened to an alloy. Iron has been found to contain within itself as much as three times its own bulk of gaseous matter. This is notably the case with meteoric iron. Dr. Graham extracted (pumped out) from a fragment of the meteoric iron of Lenarto having a bulk of 5·78 cubic centimètres, as much as 16·58 centimètres of gas, which

burned like hydrogen. On analysis it was found to consist of:—

Hydrogen .	. 8·26 cubic centimètres	=	85·68 per cent.
Carbonic oxide .	0·43 „ „	=	4·46 „
Nitrogen .	. 0·95 „ „	=	9·86 „

From 3·01 cubic centimètres of clean horse-shoe nails he pumped out, in two successive operations, 7·98 cubic centimètres of gas (equal to 2·66 times the volume of the metal), consisting of 35 per cent. of hydrogen, 50·3 carbonic oxide, 7·7 carbonic acid, and 7 nitrogen.

It is very probable that increased quantities of hydrogen in the furnace would alter these proportions, and with such alteration some changes in the properties of the iron would be effected. But here we encounter a barrier of ignorance, and come upon a subject which opens out a large field for further investigation. We know that a metal like palladium, which is capable of occluding vast quantities of hydrogen, is so changed as to form a veritable hydrogenium alloy, with properties differing considerably from those of the original metal. We have yet to learn the effect of various degrees of occlusion of different gases on the quality of pig-iron.

We have seen that the result of the action of the blast upon the fuel is to produce carbonic oxide by the direct combination of the fuel with atmospheric oxygen, and more of this same gas, plus hydrogen, by the decomposition of the water vapour carried by the blast; and that these gases, in company with nitrogen, proceed upwards through the zone of fusion, suffering little or no chemical change on the way, the conversion of CO into CO_2 occurring higher up.

Hydrogen, being an element, can only act by combination with something else; but carbonic oxide may

either combine with more oxygen, to become carbonic acid, or be decomposed or dissociated, according to its surroundings.

The researches of Deville, as already stated, show that the direct and simple dissociation of carbonic oxide by heat alone is very difficult, demanding a higher temperature than that of the blast furnace. A little reflection on the principles of dissociation expounded in Chapter III. will render this self-evident, seeing that the highest temperature of the furnace is that which is generated by the formation of carbonic oxide. These considerations, however, only apply to the direct and simple dissociation of CO into its elements—C and O.

There is another kind of breaking up of carbonic oxide, to which the name of dissociation has been applied by Mr. Lowthian Bell and others, but which I prefer, for distinction sake, to designate by the old-fashioned name of *decomposition*. Many experiments have shown that, when carbonic acid is passed over heated oxides of iron and some other metals, carbon is deposited, and carbonic acid evolved. This action is theoretically represented by the equation—

$$2\,CO = C + CO_2.$$

If carbonic oxide is, as it appears, and is usually believed to be, a binary compound of carbon and oxygen, this is something more than mere dissociation. It would be such dissociation only if carbonic oxide is a compound of elementary carbon with the compound carbonic acid, which is very improbable, and contradictory to the general laws of chemical combination.

The experiments of Mr. Lowthian Bell show that this decomposition of carbonic oxide in presence of oxide of

iron 'diminishes very rapidly as soon as red-heat is reached, and that the temperature most favourable to its production (*i.e.*, the separated carbon deposit) is between 400 degs. and 450 degs. Cent. (752 degs. and 842 degs. Fahr.).' At a bright red-heat the action is practically suppressed. It is not, therefore, a dissociation due to the separating force of heat, but a decomposition due to chemical action, merely aided by a certain degree of heat, and suppressed by a higher temperature.

With such limits to the temperature of this decomposition, we may easily understand why the CO passes on through the zone of fusion without the appearance of carbonic acid, and why, as it ascends to the less heated regions, carbonic acid makes its appearance.

But this appearance of carbonic acid commences before reaching the unreduced oxide of iron. It appears amidst the metallic iron-sponge, where also is found a deposit of carbon, apparently due to the above-described decomposition of the carbonic oxide.

Mr. Lowthian Bell has proved by direct experiment that CO passed over reduced spongy or pulverulent iron is decomposed, depositing solid carbon, and giving off CO_2; that this occurs most readily at temperatures below a full red-heat. Thus, at the temperature of melting zinc he obtained 20·3 per cent. (calculated on the quantity of iron used) of carbon deposit in 4½ hours; at 'a very dull red-heat' he obtained 23·8 per cent. in 1 hour; at a 'low red-heat' he obtained 12·3 per cent. in 2½ hours. At a bright red-heat, only ⅓ per cent. was obtained in 1 hour, and a little less after 3 hours more. Thus, as regards temperature, the conditions under which iron oxide and spongy iron are capable of decomposing the CO_2 are nearly the same.

A large number of other interesting experiments were made by Mr. Bell (far too numerous to be here described in detail), which show that, when the decomposition occurs in contact with metallic spongy iron, an oxidation of this iron takes place. He found in all cases that, when hydrogen was passed over the iron that had done this work, a certain quantity came out as vapour of water, although the same iron, previously to its exposure to the CO, allowed the hydrogen to pass over it at the same temperature without alteration.

Here, then, is an apparent paradox. Carbonic oxide, within the limits of temperature above named, reduces oxide of iron, and oxidises metallic iron—two contrary chemical actions simultaneously produced on the same elements—iron and oxygen. This paradoxical action of the CO is so fundamental to the rationale of the blast furnace that my readers will probably be willing to follow me in some theoretical speculations concerning it.

In the first place, it should be understood that the oxides of iron, like those of its near allies, manganese and chromium, display a remarkable facility in giving and taking oxygen. If a sesquioxide or sesquisalt of iron is placed in contact with substances thirsting for oxygen, it gives up some of that element to its poorer neighbour, and becomes reduced to protoxide or a protosalt; on the other hand, the protosalt or protoxide, with equal readiness, takes oxygen whenever it finds any to spare within its reach.

To illustrate this, add to a solution of protosulphate of iron (common green vitriol) some ammonia, or soda, or potash. A white or greyish hydrate of the protoxide is precipitated; this, when exposed to the air, absorbs oxygen greedily, and passes through varying shades of pale green, darker green, to black magnetic oxide; then it goes on

gradually reddening, and finally becoming hydrated sesquioxide of the well-known tint of common iron rust. This red oxide will now go black again if presented with organic or other substances that are prone to oxidise.

In the purification of coal-gas this give-and-take property is made available by passing the gas containing sulphuretted hydrogen through a layer of hydrated sesquioxide. The HS is decomposed, and water is formed, with a precipitation of sulphur, and the formation of a protosulphide of iron. When this mixture is freely exposed to the air, the protosulphide of iron is decomposed by the iron releasing the sulphur and taking up its original dose of oxygen. Thus the sesquioxide in regained, and may be used over and over again until the accumulated sulphur mechanically interferes with the oxidation of the sulphide by shutting out the free access of air. These reactions taking place at ordinary temperatures, can be easily watched and detected in the act, while those occurring at high temperatures within a furnace are hidden.

A number of other examples of the giving and taking of oxygen by iron and its oxides might be cited, but that which most directly bears upon the present problem is afforded by the action of hydrogen and water on heated oxides and heated metallic iron. If aqueous vapour is passed over red-hot iron, the water is decomposed, hydrogen is set free, and the iron is oxidised to the condition of ferrosoferric oxide (FeO, F_2O_3). In this case we have heated iron decomposing water by taking the oxygen from its hydrogen.

According to ordinary notions about relative strength of affinities, this would show that heated iron has a stronger affinity for oxygen than hydrogen has. But, on the other hand, if we exactly reverse the experiment, and

pass hydrogen over heated iron oxide, the hydrogen takes the oxygen from the oxide, reduces it to metallic iron, and forms water. Here, then, the hydrogen displays more affinity than the heated iron. The second experiment is in direct contradiction to the first. There is no mistake about these results, as both experiments have been repeated again and again by many eminent chemists, and with uniform results.

It is worthy of note that, if iron be obtained by passing hydrogen over the sesquioxide at the lowest temperature at which this decomposition can be effected (about the boiling-point of mercury), and then left to cool in an atmosphere of hydrogen, its thirst for oxygen is so strong that, if exposed to the air, it instantly takes fire spontaneously, and is converted into sesquioxide (*see* Magnus, 'Poggendorf's Annalen,' vol. iii. p. 81, and vol. vi. p. 509; also Stromeyer, in the same volume, p. 471). But if iron be reduced by oxygen at a red heat, it does not thus take oxygen until heated nearly to redness.

The theory I venture to suggest, is that in the blast furnace both these actions occur, and operate upon the carbonic oxide: on one side it comes in contact with metallic iron in a state of chemical activity, which robs it of its oxygen, and precipitates the flocculent carbon; on another side it meets with oxide that gives up its oxygen, and converts the CO into CO_2. As both of these actions are found to take place within the same range of temperature, it is quite possible that both may occur in the same part of the furnace—that is, at the part where this carbon deposit is found, and which has the temperature that outside experiments show to be most favourable for both of these contradictory reactions.

Another example of the chemical inconsistency of iron

is that presented by its 'passive condition.' If a piece of iron be immersed in nitric acid of specific gravity about 1·35, oxidation and solution immediately occur, the action proceeding quite violently; if, in the midst of this, the iron be touched beneath the surface of the acid with a piece of gold, or platinum, or carbon in the form of plumbago, the action suddenly ceases, and the iron may remain for days in the acid. If a second wire be made to touch the first, and is then immediately immersed in acid, it is found to have acquired the passive condition; this second may infect a third, the third a fourth, and so on. If these are now removed from the acid, and exposed to the air for a few seconds, they regain their active condition, and are rapidly oxidised and dissolved. If into acid containing a piece of passive wire a second ordinary wire is plunged, not in contact with the first, the second is active, while the first remains passive; but if the second is now made to touch the first, both become active. Thus, if contact is made before immersion of the second, both become passive; if after immersion, both become active.

Various explanations of these chemical vagaries have been attempted. Some have supposed that the action is voltaic, or connected with the magnetism of iron; others, that it is due to an adherent and protective film of oxide, or of non-combined oxygen. But however this may be, it is a fact that the same piece of iron may at one moment display a strong affinity for oxygen comparable to that of zinc, and at another it may resist a powerful oxidising agent after the manner of gold or platinum.

In Mr. Bell's experiments, CO was passed over finely-divided, pulverulent iron, which had been reduced from the sesquioxide by hydrogen, the result being the deposition of solid carbon, and the formation of CO_2; and, besides

these, the formation of a certain quantity of iron oxide, supposed by Mr. Bell to be in a very low state of oxidation. But this is uncertain, as the oxidation of a small proportion of the subsequent supplies of hydrogen may have been due to a small proportion of highly oxidised iron intermingled with metallic iron.

The rationale of this experiment I suppose to be this: First of all, the pulverulent iron, by virtue of its strong affinity for oxygen, reduces a portion of the CO, by combining with its O, and throwing down its C; then comes another portion of CO over the oxide of iron thus formed. This takes the O from the iron oxide, and is thus converted into CO_2; and these alternations of action continue so long as the temperature favourable to both is maintained. The same in the blast furnace, where the iron has been reduced from the oxide of the ore higher up, and is now meeting the CO while in a spongy condition similar to that of the reduced iron in the tube experiment.

There is a difficulty in conceiving when and why the reversion of action should occur; when and why the iron which has been, so far, taking oxygen from CO should become satisfied, and now reject the oxygen it had previously obtained. Something like the alternation of the active and passive condition of iron with nitric acid may occur with both the metallic iron and its oxide; so that, when the oxidising action starts, it runs on with a certain momentum which carries it, like the swing of a pendulum, beyond the neutral degree of oxidation, and then an excessive oxidation is effected, which presently starts a return swing, of reducing action, which proceeds to a similar excess in the opposite direction, and so on continuously. I think it very probable that the deposited carbon may be a confederate in this, seeing that the contact of such carbon

is capable of arresting the oxidising action of nitric acid upon iron.

Proceeding upwards in company with the gases of the blast, we arrive now at that part of the furnace where carbonic acid makes its appearance in consequence of the reactions described in the last chapter. With the carbonic acid is also the finely-divided deposit of solid carbon due to these same reactions. The iron at this part of the furnace is completely reduced from the ore, and exposed to a heat nearly corresponding to that of a cementing furnace.

The effect of this is evident enough: Cementation must take place; the refractory iron combines with carbon, and its melting-point is thereby lowered, for, as we all know, compounds of iron and carbon increase in fusibility with increasing quantities of combined carbon.

But this is not all.

With the ores there was silicic acid, upon which the powerful reducing agencies of hydrogen and carbonic oxide, aided by the direct dissociating force of heat, have operated; and these reducing agencies are further assisted by the facility with which the iron itself takes up any nascent silicon at the moment of its separation from the oxygen. Thus, we have silicon combining with the iron simultaneously with the carbon. Silicon acts like carbon, even more effectively, in lowering the melting-point of iron. The quantity of carbon and silicon commonly taken up amounts to as much as 5 per cent.

When the ore is a clay-ironstone, containing remains of vertebrate animals, as described in Chapter II., the phosphate of lime is decomposed, the lime unites with the silica to become silicate of lime, the phosphoric acid is dissociated, its phosphorus goes to the iron, and still

further increases its fusibility. Besides these, some sulphur is taken from the pyrites in the coal, and thus the nearly pure and practically infusible iron of the iron-sponge is converted into a mixture of carbide, silicide, phosphide, and sulphide of iron, or pig-iron, of comparatively easy fusibility.

Thus the 'zone of fusion' marked in Mr. Lowthian Bell's diagram is determined, not entirely by the increase of temperature, but also by the combinations that have taken place above it.

The reduction of temperature which occurs as we ascend the furnace is due to the work done by the heat in dissociation and volatilisation, and also to the fact that it is continually diffused over larger and larger quantities of material. These cooling operations are rapidly proceeding from the zone of fusion upwards to the 'bright red' heat zone, where the expansion of width of the furnace rapidly increases the area of diffusion of the heat. It then goes on upward into the 'full red' zone of absorption, down which is creeping the great mass of material originally cold.

At the upper part of this—marked 'red-hot' in the diagram, Mr. Bell found the limestone to be decomposing. This decomposition is effected at the expense of a large amount of sensible heat, seeing that not only has the carbonate of lime to be dissociated into caustic lime and carbonic acid, but this latter has to be expanded from the state of a solid to that of a gas. A proportionate lowering of temperature must, therefore, take place where the heat is engaged in doing this work. I have taken the liberty of bracketing together Mr. Lowthian Bell's two zones of 'reduction' and 'limestone decomposition,' believing that the reduction is not completed until a full

red heat is attained, though it commences, as Mr. Bell has proved, at a lower temperature than was formerly supposed.[1]

We now come to the upper contraction of the furnace, where mere heating of the fresh, cool materials of the charge is effected—which heating is aided by the shape of this portion of the furnace, as its upward narrowing necessarily concentrates the heat coming upward from a wider to a narrower area of diffusion.

Merely looking down into the flaming throat of a blast furnace naturally suggests the idea that the fuel charged with the ore is there, and at once burned in such wise as to give out a furious heat. This, however, is far from being the case. Excepting at the top surface of an open-throat furnace, there can be no such immediate combustion of the fuel, simply because there is no free oxygen to combine with it in the upper part of the furnace.

The oxygen of the blast, as I have already shown, is used up as free oxygen in the course of a very short portion of its upward progress, and therefore any oxidation that occurs above this (such as that of the hydrogen and carbonic oxide in reducing silica, ore, &c.), takes place at the expense of a corresponding reduction or dissociation of some compound of oxygen; and such reduction or dissociation is accompanied with a loss of temperature or sensible heat corresponding to that which is given out in the oxidisation of the reducing agent.

Analyses of the gases issuing from the top of blast furnaces have been made by Playfair, Tunner, Bunsen, Ebelman, Scheerer, and others, with considerable varia-

[1] I first took this liberty when writing my contribution to Stanford's 'British Manufacturing Industries,' vol. i., published 1876; afterwards, in my 'Cantor Lectures on Iron and Steel;' and now find full justification in the fact that Mr. Bell has since adopted this modification of his original diagram.

tions of result, according to the construction and charge of the furnace; but all agree in showing an absence of uncombined oxygen. The following is the mean result of several of these analyses:—

Nitrogen	56·45
Carbonic acid	11·16
Carbonic oxide	25·83
Marsh gas	0·98
Olefiant gas	0·12
Hydrogen	5·46

Here we have about two-thirds of incombustible materials (nitrogen and carbonic acid), and about one-third of combustible gases (carbonic oxide, marsh gas, olefiant gas, and hydrogen)—a mixture in which free oxygen could not exist, as, at the temperature of the furnace, it would combine with one or other or all of these combustible gases. A little reflection on what has preceded will show that such must be the case from the top of the furnace down to but a short distance from the blast itself.

Thus, all the heat distributed throughout the great mass of fuel, &c., in the blast furnace, is generated at the lower part, within but a few feet from the tuyères. Were it otherwise, if the combustion of the fuel were going on in the middle and upper part of the furnace, its proper shape would be that of a column contracting downwards in correspondence with the diminishing bulk of its contents.

Experience has shown that the opposite form—viz., contracting upwards—is advantageous; and one of the causes of this advantage is, probably, that such a shape moderates the rapidity of upward cooling; or, what is the same thing, causes the gradual heating of the descending charge to

more slowly, and to do its work more

oxygen in the issuing gases enables
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must be nearly the same. If they are not carried out of the furnace at the top, they must follow the charge to the bottom, and, unless they are inert substances, must do something on the way. The quantities and composition of this fume are, therefore, matters of interest.

Mr. Lowthian Bell's experiments on this subject are very interesting so far as they go, but, as he says, 'a greater number of observations are required.' He erected a steam-pump, and drew, through a foot or two of water, the gases from a furnace 60 feet in height. The condensed matter was analysed by M. Henri Brivet in the Washington Laboratory, and was found to contain 52·67 parts soluble in water, and 47·17 insoluble. The soluble matter contained :—

Silica	1·37	parts in the 52·67
Alumina	12·20	
Lime	trace	
Magnesia	trace	
Chlorine	0·57	
Sulphuric acid	0·59	
Oxide of zinc	4·58	
Carbonates of potash and soda	22·90	
Loss in heating	10·46	

The 47·17 parts of insoluble matter consisted of :—

Silica	11·00
Alumina and sesquioxide of iron	10·76
Lime	2·06
Magnesia	trace
Oxide of lime	12·28
Carbonic acid	7·00
Alkaline salts	3·07

The quantity of this solid matter that is precipitated from the escaping gases is larger than might be supposed. Mr. Lowthian Bell found that, from a furnace 60 feet

take place more slowly, and to do its work more effectively.

The absence of oxygen in the issuing gases enables them to be carried away as fuel, and used for heating the blast, boilers, &c., by supplying them with a suitable quantity of air when they arrive at their destination.

The composition of the issuing gases, as above stated, only includes the permanent gases. Besides these, there is a variable amount of condensible matter, due to the sublimation of volatile solids in the furnace. Its existence is indicated by the white clouds that float over iron-making districts, especially those where Cleveland ores are reduced. The miserable condition of the vegetation below these clouds is, doubtless, due to the falling down of the minute particles of saline matter of which they are constituted. When a cold iron bar is driven into the lower part of a furnace, and withdrawn, it is found to be coated with a white, saline incrustation. This appears to be due partly to salts in a state of fusion, and partly to saline vapours. The quantity of these vapours intermingled with the gases finally issuing from the top of the furnace is sufficient to form an incrustation that renders necessary a periodical cleaning of the hot-air pipes that are fired with the waste gases.

A greater amount of this 'fume' is emitted from small furnaces than from larger, doubtless on account of the deposition that occurs on the greater quantity of upper material in the latter. Mr. Bell found, on two occasions, 77·31 and 59·09 parts were given off from a furnace of 48 feet in height, against 27·24 and 19·54 from a furnace of 80 feet high, both estimated upon the same quantity of iron made. This difference is suggestive. With similar ores, fuel, and flux, the actual production of such salts

must be nearly the same. If they are not carried out of the furnace at the top, they must follow the charge to the bottom, and, unless they are inert substances, must do something on the way. The quantities and composition of this fume are, therefore, matters of interest.

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Alkaline salts	3·07

The quantity of this solid matter that is precipitated from the escaping gases is larger than might be supposed. Mr. Lowthian Bell found that, from a furnace 60 feet

high, it amounts to 2·6 cwt. per ton of metal produced. This indicates a difference of about 1½ cwt. per ton between the quantity given out by the 48-feet furnace and the 80-feet furnace; or, otherwise stated, the tall furnace carries down 1½ cwt. more of these salts to the ton of iron than does the shorter furnace.

Those who believe in puddlers' 'physic' may easily suppose that the quality of the iron may be affected by such difference, as some of the salts are those which enter into the composition of some of the most popular of these physics—the carbonates of potash and soda, for example. Quite a multitude of patents have been secured for the addition of such salts to the charge of the blast furnace, or to the pig in its subsequent treatment, the inventors evidently being quite ignorant of what I have explained in the above. Whether this 'fume,' or 'flue dust,' affects the iron or not, it must influence the composition of the cinder. These are subjects still open for further investigation.

There is another subject also closely connected with them—that is, the action of cyanogen and alkaline cyanides in the blast furnace. Cyanogen, as most of my readers know, is a compound of carbon and nitrogen, the discovery of which, in 1814, by Guy Lussac, had an important influence on chemical theories, inasmuch as it behaved in its combinations as only elementary substances were then supposed to do. It is a very powerful reducing agent, and it is formed, somehow, by the union of the nitrogen of the blast with some of the carbon in the furnace.

This in itself is interesting, as the nitrogen of the atmosphere is usually so inert that indirect or violent means are necessary to force it into combination with

anything. Much discussion has arisen on the question whether free cyanogen gas exists at all in the blast furnace, or whether it is there only in combination with the alkalies. The mere bringing together of carbon and nitrogen, whether hot or cold, will not produce cyanogen; but if nitrogen be passed through a tube in which a mixture of carbonate of potash and charcoal are heated, cyanide of potassium is formed; or carbonate of soda may be thus used for the production of cyanide of soda. In the blast furnace we have heated carbon in abundance, and, as the above analyses of the fumes show, there are also the carbonates of potash and soda; thus, the formation of alkaline cyanides by the action of the nitrogen of the blast upon these is quite intelligible.

Bunsen and Playfair estimated that, in every cubic mètre of gas at a height of 2·75 feet above the level of the tuyère in the Alfreton furnace, there were 8 or 10 grammes of cyanide of potassium per cubic mètre of gas. Mr. Lowthian Bell's experiments indicate about 4 lbs. of cyanogen per ton of iron produced, which, combined with potassium, would amount in round numbers to 10 lbs. of the salt. The alkaline cyanides are reducing agents, but whether they act with any practical effect in the furnace is still doubtful. Mr. Lowthian Bell says: 'The whole subject is one upon which my mind is by no means made up.' I am in the same state of mind as Mr. Bell, and therefore leave the problem as enunciated, but not solved.

CHAPTER VII

THE THEORY OF PUDDLING

As already explained, the modern blast furnace requires, as one of the conditions of its action, the introduction of certain impurities, such as silicon and carbon, in order that the iron-sponge produced in the upper part may become fused and run out as melted metal below. The fusibility is further increased by the sulphur obtained from the pyrites in our coal fuel, and by the phosphorus commonly existing in the ores which were deposited after the vertebrated animals made their appearance on the earth, and left behind them the phosphate of lime of their bones. The ancient and primitive ironmakers escaped both of these impurities by using charcoal fuel and the purer oxides of more ancient formation.

Thus, the modern blast furnace necessarily thrusts upon the modern ironmaster the problem of removing those impurities which his mode of reduction has added to the product he calls pig-iron, but which is really a mongrel steel, containing too much carbon to be weldable, and too much of the other impurities to be malleable, or have any degree of workable toughness. Its simple merit is fusibility, and hence it may be used for foundry purposes, provided it is not excessively charged with silicon, sulphur, or phosphorus.

The following is the mean of analyses of thirty good

brands of English pig-irons used at the Atlas Works, Sheffield, and analysed in the laboratory of the works by myself:—

Combined carbon	0·916	Total carbon,
Graphitic carbon	1·918	2·834
Silicon	1·810	
Phosphorus	0·332	
Sulphur	0·253	
Manganese	1·280	
Iron by difference	93·491	
	100·000	

The following shows the composition of a Cleveland pig made from ores containing much of the organic phosphates above named:—

Combined carbon	0·80	Total carbon,
Graphitic carbon	1·00	1·80
Silicon	2·23	
Sulphur	0·27	
Phosphorus	1·30	
Manganese	0·71	
Iron by difference	93·69	
	100·00	

The problem presented by these impurities appears, at first sight, simple enough. Silicon, carbon, sulphur, and phosphorus are all readily-combustible substances. Nothing further seems, therefore, to be needed than to melt the crude material, and while thus heated to expose all parts freely to the air, and thus oxidise or burn out these impurities. Previous to Cort's invention of the puddling process, this was the only method of purification of pig-iron that was practically carried out, though not on the basis of any such theoretical considerations, for it was in use long before the discovery of oxygen and the existence of the modern theory of combustion.

Various kinds of 'fineries,' or 'refineries,' were in use, but they may be all included in two classes—viz., the open-hearth fineries, in which the crude metal is melted down into a square, shallow, open hearth, the surface of which is subjected to the action of powerful blasts obliquely projected upon it by means of tuyères. A certain degree of circulation of this fluid metal is thus effected, and as fresh material comes to the surface it is subject to the oxidising action of the blast. When the action has been carried far enough, the fluid metal is tapped into a shallow trough of casting-sand, where it cools into the form known as 'refined' iron, or 'plate' iron, as distinguished from 'pig' iron. This is the form of finery furnace still used in this country, though not nearly to the same extent as formerly.

The bloomery, of which there are many forms, is of great antiquity, and is still used where rich ores, free, or nearly free, from phosphorus, are reduced by charcoal free from sulphur. The crude iron is placed in the upper part of a charcoal fire, or upon an upper hearth, and, with the fuel, is subjected to the action of a blast. It melts very gradually, and, as it descends drop by drop, its carbon is subjected to the oxidising action of the blast, the final result being the formation of a ball, or bloom of iron so nearly pure as to be practicably infusible, and only requiring squeezing under the hammer to become good malleable iron, improvable by re-heating.

The small furnaces now used in this country for making charcoal scrap-iron belong to this class; but instead of being charged with crude, or pig-iron, they are charged with iron-scrap. What, then, is wrong with these bloomeries? Why have they so nearly fallen into disuse in this country, and been superseded by the puddling process for the production of malleable iron?

These questions bring us directly upon the theory of puddling. In the first place, let us inquire into what takes place in the first class of finery, or 'running-out fire,' as it has been called, where the refined metal is cooled down from the fused state.

I have made several analyses of pig-iron before refining, and the plate-iron resulting from refining, and find that nearly all the silicon is oxidised, and carried away as fusible cinder, by combining with the oxidised manganese of the pig, and with some of its oxidised iron, or with calcium, if any were there. Thus, one of the impurities of the pig was proved to be removable by simple oxidation.

Some of the carbon was also oxidised, the quantity depending upon the length of time during which the blast was continued.

Another change always occurred—viz., the conversion of the graphitic carbon into combined carbon, or grey iron into white iron. Thus we have an iron well adapted for foundry purposes, the combined carbon giving it fusibility, while the removal of the silicon diminishes its brittleness.

But the sulphur and phosphorus remain practically unaffected. These results, which are fully in accord with those obtained by many others who have made similar analyses, show that something more than mere direct oxidation is necessary for the purification of ordinary British pig-iron containing a mischievous quantity of sulphur and phosphorus.

This was not understood in 1855 and 1856, when Mr. Bessemer was struggling with the early stages of his invention, nor was it made at all clear until some time afterwards. It was, however, brought out very distinctly by analyses of specimens of Bessemer metal that gave

way under the hammer, by cracking at their edges or breaking up altogether.

It then became quite clear that no amount of mere exposure of the heated pig-iron to air, even though it be blown through the melted metal, and accompanied with the furious agitation that occurs in the Bessemer converter, can effect the oxidation of the sulphur and phosphorus, without at the same time oxidising the iron itself. The Bessemer process was originally based on the theory that the complete purification of pig-iron could be effected by mere oxidation. At this time, and long after, the puddling process was regarded and described as a method of oxidation. This will be seen by reference to chemical and technological treatises published prior to 1870, and even later.

At first the oxidation was attributed simply to the air acting on the surface, and the business of the puddler was described as stirring up the molten metal 'so as to expose fresh surfaces to the oxidising influence of the draft' (Tomlinson's 'Cyclopædia of Useful Arts,' 1854), whereby the silicon, carbon, sulphur, and phosphorus were simply burnt away, and the metallic iron left unburnt.

In Sir Henry E. Roscoe's 'Lessons in Elementary Chemistry' is the following very crude statement: the formation of 'large lumps, or balls,' by *rolling*, will amuse ironworkers. Sir H. E. Roscoe's work is highly recommended as a text-book.

'In order to obtain wrought from cast iron, the latter must undergo the process of "refining" and "puddling.' These consist essentially in burning out the carbon, silicon, sulphur, and phosphorus, by exposing the heated metal to a current of air in a reverberatory furnace; the melted cast iron becomes, first coated with a coat of oxide, and

gradually thickens so as to allow of its being rolled into large lumps or balls.'

The next step in the progress of the generally-accepted theory was that the iron itself was oxidised by the air, and the oxide thus formed gave up its oxygen to the carbon, &c. Thus Wagner ('Handbook of Chemical Technology,' translated by Crookes, 1872) says: 'The theory of the puddling process is the following:—The current of air which comes into contact with the molten iron causes the formation of a not inconsiderable quantity of protoperoxide of iron, the oxygen of which eliminates the carbon contained in the pig-iron in the shape of carbonic oxide, which burns off with a bluish flame.'

This theory, variously stated by various writers, still includes only oxidation, indirectly effected by the oxygen of the air playing on the surface of the molten metal.

An important stride was made in this oxidation theory when the action of the fettling materials as oxidising agents was recognised. To the best of my knowledge and belief, this recognition was first made by a working puddler, who published a little pamphlet on the subject. I regret my inability to do full justice to this writer by recording his name and quoting his own words, for my acquaintance with his work was made, some twenty years ago, by a loan of the pamphlet, which was duly returned to the lender, who I am now unable to find; and my note of the title of the pamphlet and name of its author are also lost. The essay is one of considerable merit and interest, deserving a better fate than its present oblivion.

In reference to this, it should be remembered that in Cort's specification, dated February 13, 1784, no mention is made of any fettling material. He used sand bottoms, and it was not until a later period that the so-called 'dry

puddling' was superseded by the introduction of 'wet puddling,' or 'pig boiling,' a modification depending essentially upon the addition of a lining of oxide of iron in some form, which oxide is reduced to metallic iron by giving up its oxygen to the carbon of the pig, and probably also to its silicon, whereby these impurities are removed, and at the same time the yield of finished metal is increased. The puddling-furnace thus becomes a reducing as well as a purifying or refining apparatus. By using rich hematite as a fettling, and working the rabble well along the bottom, it is quite possible to bring out a weight of puddled bar exceeding the weight of the original charge of pig. I have frequently done this (with the aid of an intelligent workman), in order to test severely this element of the theory of puddling.

The chemistry of 'bull-dog' and its preparation becomes interesting and intelligible when this is understood. In its raw state, as refuse tap cinder, it is an impure silicate of iron, the protoxide of iron being firmly combined with the silicic acid as a fusible glass, which, if used as fettling in this state, would simply melt, and float up to the surface. It is prepared or converted into bull-dog by roasting it in an oven like a limekiln. The protoxide takes up an additional dose of oxygen, and leaves the silicic acid, thus becoming a *mixture*—not a compound—of sesquioxide of iron and uncombined silicic acid.

This sesquioxide, when used as fettling, is reduced to protoxide, giving up its oxygen to the carbon of the pig, as in the case of the hematite fettling. My experiments indicate that it does not contribute to the yield, but returns to the silica when reduced to protoxide. I found that, with a given pig, a more fluid cinder was obtained when working with bull-dog fettling than with hematite.

In my experiments with the latter only, and with a pig containing but little silicon, the puddlers had to work harder, and the time for working the heat was greater. They complained that the iron worked 'dry' in these long, experimental heats, using the word in a double sense: the cinder lacked silica, and the puddlers lacked beer to compensate for the extra labour.

The 'boiling' is, unquestionably, due to the evolution of carbonic oxide *below* the surface of the melted metal, for the formation of which oxygen is supplied by the fettling.

I now come to the question of whether such supply of oxygen below, as well as above, is sufficient to account for the removal of sulphur and phosphorus that actually occurs in the puddling process, or whether something more than mere oxidation occurs. As already stated, no amount of injection of air into the melted pig has any sensible effect on these impurities as they ordinarily exist in pig-iron. A very great excess may be reduced to about the quantity found in ordinary samples, but when it has reached this amount it there sticks so firmly that the iron itself must be oxidised rather than either of the intruders.

The necessity of discussing this question fully has been strongly and painfully impressed upon me in the course of a work upon which I have been for some years past engaged, viz., 'A History of British Invention in the Manufacture of Iron,' published serially in 'Iron.' The history presents a melancholy crowd of examples of wasted ingenuity, wasted energy, wasted capital, and consequent vexation, disappointment, misery, and ruin, all arising from the theory that mere oxidation can purify British pig-iron, and a too faithful reliance upon the ordinary text-book statement that steel may be regarded 'simply as

iron carbonised in degrees intermediate between malleable and cast-iron.'

The specifications of costly patents based on these false theories, if collected together, would fill a thick volume. In many cases the patentees have been workmen, and others who have sacrificed the savings of years in securing protection and striving to bring out their hopeless inventions. I shall have to refer again to these when on the subject of steel, as, in nearly all cases where this oxidation theory has been the source of delusion, the inventors have devised some means of partial, as well as of complete oxidation of the carbon, on the assumption that 'crude iron and steel only differ from each other in the proportion of carbon they contain.'[1]

It is perfectly natural that such a theory should have prevailed, seeing that it had a natural historical origin, and once was very nearly sound—quite sound if we neglect the distinction between the nearly-resembling elements, silicon and carbon. When crude iron was made from the nearly pure oxides reduced by charcoal, its impurities were carbon and a little silicon. Such iron, treated with any simple oxidising agent, first gave up its silicon by oxidation, then its carbon. If the oxidation were stopped when all the silicon was oxidised, and a due proportion of the carbon remained, the result was steel; when the oxidation was carried so far that less than $\frac{1}{3}$ or $\frac{1}{4}$ per cent. of carbon remained, the result was malleable iron.

It was the British manufacture of pig-iron from the clay-ironstones containing phosphates, and the British use of coal in which are crystals and laminæ of pyrites, that

[1] Mushet, *Papers on Iron and Steel* (1840), p. 526.

falsified this simple theory, and rendered the puddling process necessary.

The old theory survived the new process,[1] and was applied to it with an almost irresistible plausibility—a plausibility arising from the fact that it is true to a limited extent, but is not the whole truth. Oxidation does take place, and is an important agency in puddling, but it is not the only one.

Even the oxidation of the carbon and the silicon is by no means complete. Careful analysis shows that the best wrought iron contains a little carbon and some silicon. Gmelin ('Handbook of Chemistry,' vol. v. p. 183, Cavendish Society's edition) says: 'Bar iron still contains ½ per cent. of carbon.' (This is excessive. Modern steel rails have about this quantity). Miller says, $\frac{1}{400}$ to $\frac{1}{200}$ of its weight of carbon, and $\frac{1}{500}$ of its weight of silicon. Other authorities name other proportions, as they well may do, seeing that different samples vary so greatly.

In the ordinary course of puddling, the contents of the furnace are drawn into two, three, or more balls—usually three. I have made several experiments by determining the percentage of carbon contained in bars made from each of these balls, and have always found that the bar from the first ball contains more carbon than that from the second, and the second more than the third. From 0·15 to 0·25 per cent. was found in the bar from the first ball. In the case of the larger quantity, the bar from the second

[1] In Watts's *Manual of Chemistry* (one of our best modern text-books) I find the following: 'The general nature of the change in the puddling-furnace is not difficult to explain. Cast iron consists essentially of iron in combination with carbon and silicon, and these compounds, when strongly heated with iron oxide, undergo decomposition, the carbon and silicon being oxidised at the expense of the oxygen of the oxide.'

ball usually contained about half as much as the first; the third, but a trace. When, however, the first ball contained less, the difference between the first and the second was smaller, and the third had still but a trace—just sufficient to show itself, but too small to be quantitatively estimated by the method of analysis used.

The cause of this is obvious enough: the spongy iron undergoes oxidation during and after 'balling up,' in spite of all the puddler's efforts to muffle his fire and cover the ball with cinder; and as the balls wait their turns for the hammer, the second has more of this exposure than the first, and the third more still. On this account it is desirable, wherever practicable, to weld all the balls of a given heat together.

The want of homogeneity which is so common a defect of wrought iron is largely due to this difference between different parts of the same heat, the iron of the first ball being, of course, harder than that of the last. Piling, re-heating, and re-rolling are partial remedies, as they mix the variously composed samples together.

Further studies of this subject have led me to the conclusion that it is impossible to remove all the carbon from iron by any known oxidising process, for the simple reason that, before the carbon has all gone, the oxidation of the iron itself commences, and the result of carrying on the oxidation of the carbon beyond a certain extent is the production of 'burnt iron'—*i.e.*, a sample in which minute particles of oxide are entangled with the metal (*see* Chapter XIV.).

Pure iron is never produced by any commercial manufacturing process; and, even to the chemist in his laboratory, where the cost is not considered, the production of only a small museum specimen is a very difficult problem,

which is best solved by first precipitating pure oxide of iron from the solution of a purified salt of iron, and reducing this with pure hydrogen gas. Even this contains occluded hydrogen, or hydrogen in a solid, and probably metallic, state, and is, therefore, an alloy of iron and hydrogenium.

An interesting and instructive series of experiments was made at the Atlas Works, Sheffield, above twenty years ago. In the manufacture of armour-plates (as then produced before 'sandwiching' with steel was practised), success depended upon obtaining iron as soft as possible—*i.e.*, as free from carbon, silicon, sulphur, and phosphorus as it could be made, the presence of any of these impurities hardening the plate, and rendering it liable to crack when tested by the point-blank shots at Shoeburyness.

As these plates, many weighing about 30 tons, were built up by welding together puddled balls, which usually weigh less than 1½ cwt. each, a great deal of such building up, piling, re-heating, and re-rolling is demanded. In the course of this manufacture, the traditional dogma of the forge, that re-heating, cutting up, piling, and re-rolling continually improves the quality of the iron, was seriously discredited, for some of the much-worked armour-plates proved to be very bad, while ordinary boiler-plates made from the same quality of bars were excellent.

This suggested the question of whether there is any practical limit to the improvement obtained by repeated rolling, shearing, piling, re-heating, and re-rolling of iron, and the answer was obtained by very carefully rolling thick iron plates, then testing a piece of each by bending and fracture. The body of these plates was then cut up, piled, welded, and re-rolled; these second plates were similarly tested, treated like the first; and so on.

The bending and fracture tests indicated improvement up to the fifth, and in some cases to the sixth or seventh, rolling. After this a rapid deterioration occurred: the plates gave way under the bending tests, and although they still displayed a very fibrous structure, the silvery lustre of the fibres was diminished; they had a dirty appearance, which increased with every rolling. A good magnifier showed that this was due to minute black specks distributed between or among the fibres. I examined these and other similar samples, and found that the specks were particles of black oxide of iron, and this suggested the theory that ordinary good wrought iron must contain a certain proportion of carbon—just a sufficient quantity to protect the iron itself from oxidation when heated, by the carbon taking up the oxygen itself, instead of allowing the iron to do so. This theory was treated as rank heresy by the chemists of the period, but I tested it by a number of other experiments, some of which will be described and discussed in future chapters.

Silicon, when associated with iron, is more easily combustible than carbon. This may be proved by making analyses of the metal taken from a Bessemer converter in different stages of the blow. It will be found that the silicon is first oxidised, and while its quantity is considerable it appears to protect the carbon; then, as it is burnt down to a smaller proportion, the oxidation of the carbon commences.

Does mere oxidation remove the whole of the silicon? This question is not so easily answered by direct analysis as the corresponding question applied to carbon, simply because the detection of small quantities of silicon is more difficult than in the case of carbon. The formation of a scum of silicate of manganese on the top of the melted

steel in crucibles to which oxide of manganese has been added indicates the presence of a residuum of silicon even in the finest qualities of charcoal-iron, though in this case it is possible that there may be another source of the silicon—viz., the melting-pot itself. If, however, *all* the silica that comes up were derived from the pot, it is difficult to understand how the oxide of manganese improves the steel, one of the conditions of such improvement being that none of the manganese shall remain behind. It is not by what it adds, but by what it takes away, that the manganese benefits ordinary steel.

It may appear that these details are carrying us away from the subject of the theory of puddling, but we shall soon see that such is not the case. My object is to bring out an important principle, that has hitherto been quite overlooked, or, rather, misunderstood and ignored.

As already intimated, the first revelation of the fact that mere oxidation is insufficient for the production of merchantable iron from ordinary English pig-iron was made in the early stages of the Bessemer struggle. Samples of pig-iron were analysed, then fused, run into the converter, and there subjected to the extreme torture of oxidation by torrents of air pouring through the liquid metal from below. The result was tested mechanically, and subjected to chemical analysis. The mechanical tests were unsatisfactory, and chemical analysis revealed a removal of carbon and silicon, with a persistence of sulphur and phosphorus.

I well remember the excitement that prevailed in the Black Country at the time, and the samples that were handed about of the new steel which, when hammered either hot or cold, fractured at its edges. The results of the analyses were published in Birmingham, Wolver-

hampton, Sheffield, &c., showing the same percentage of sulphur and phosphorus in the steel as in the crude pig-iron.

The inference from this was that sulphur and phosphorus, though so eminently combustible when alone and outside of the iron, are quite different within iron, or when combined with it; while carbon and silicon, even when combined with iron, display their usual combustibility, and are, therefore, removable by oxidation.

This has been repeated over and over again in many forms of words, and is still taught as established, indisputable science. Nevertheless, I venture to dispute it, and to affirm that there is no such difference between the behaviour of the sulphur and phosphorus and that of carbon and silicon, under corresponding circumstances of oxidation.

My contention is this: that carbon, silicon, sulphur, and phosphorus (I might add, calcium), are all similarly capable of oxidation when associated with iron in considerable proportions; that down to a certain point this oxidation proceeds in such a manner as to remove these impurities, but that beyond this the oxidation of the iron itself occurs simultaneously, and thus the oxygen ceases to act as a purifying agent.

Reference to the mean composition of the thirty brands of pig-iron given on page 125 will show that, in subjecting such pigs to a Bessemer blow, or other oxidising process, we start with nearly 3 per cent. of carbon and nearly 2 per cent. of silicon, while we have but $\frac{1}{4}$ per cent. of sulphur and $\frac{1}{3}$ per cent. of phosphorus. As above stated, we may finish, even after puddling, with nearly as much carbon as this beginning proportion of sulphur or phosphorus; or, if we simply oxidise, as in the finery or

Bessemer blowing, and stop this before any burning of the iron commences, we shall find remaining behind quite as much of silicon and carbon as of sulphur and phosphorus. The practical difference of the result is due to the fact that ¼ per cent. of phosphorus or of sulphur has a far more damaging effect on the iron than the same proportion of carbon or silicon.

On the other hand, if we were to start a Bessemer blow with 2 and 3 per cent. of sulphur and phosphorus, and ¼ and ⅓ per cent. of silicon and carbon, the probable result would be the removal of sulphur and phosphorus, and the persistence of carbon and silicon. I say *if*, not having actually tried the experiment in this form, but have witnessed the removal of such excess of both sulphur and phosphorus by other means of simple oxidation that will be described as I proceed. In the meantime, I may mention that this was done by the 'Heaton process,' in several experiments, independently witnessed by different chemists, who analysed the pig-iron and the final product. To avoid repetition, I merely name the fact now, as the details will have to be stated when I reach the subject of direct steel-making.

The above-stated facts, and a multitude of others that might be added, prove, I think conclusively, that the purifying action of oxygen on pig-iron is limited to the removal of only a certain proportion of the silicon, carbon, sulphur, and phosphorus, small residual quantities of these adhering so pertinaciously to the iron that they cannot be burnt away without also burning the iron itself. In the case of the carbon this residuum does no harm—is, rather, advantageous; the silicon residuum does very little harm beyond mere hardening, but similar proportions of sulphur and phosphorus are decidedly mischievous. This is so

well understood that I need not here state the evidence upon which the conclusion is founded.

But skilful puddling does remove nearly the whole of this obstinate residuum. What, then, is the rationale of this efficiency if it is not due, as was so generally believed, to mere oxidation?

Dr. Percy has suggested that a 'liquation,' or sweating-out of these impurities may take place. He says that, 'owing to the formation and persistency of these pasty lumps in the puddling-furnace, which, when collected into balls, extend considerably above the bath of cinder, opportunity is afforded for the liquation or sweating-out of any fusible compounds of iron, such as the phosphide; and it is in this manner that I conceive the removal of the phosphorus may, in a great measure, be effected. The following fact, confirmed by the experiments of my friend, Mr. Abel, of the Royal Arsenal of Woolwich, would seem to favour this view. When pig-iron containing phosphorus in sensible quantity is remelted and cast, that portion of the metal which is solidified last will be found to be richer in phosphorus than the other portion of the casting.'

According to this theory, the work of separation is effected where the iron is exposed to the air outside the cinder, and thus the efficiency of the agitation in rabbling, &c., is due to the extent of such exposure thereby obtained.

My own theory of puddling was roughly sketched in vol. i. of Stanford's 'British Manufacturing Industries' (1876), and afterwards more fully expounded in my fourth Cantor Lecture to the Society of Arts, delivered February 7, 1876. I here quote this exposition as published in the Society's Journal at the time, and in their collected series of Cantor Lectures.

'I have devoted some attention to this subject, and offer the following as my own theory of the process of puddling:—

'1st. That pure iron, itself practically infusible, becomes, when sufficiently heated, soluble in its own more fusible compounds—such as its silicides, carbides, phosphides, &c.—and that pig-iron is mainly composed of such a solution.

'2nd. That the carbon and silicon are oxidised in the early stages of puddling, and thus the solvent is diminished, and the iron is precipitated as granules; but it is not yet pure, each granule being enveloped in fusible sulphide and phosphide, too small in quantity to effect solution of the iron, but adhering to it so firmly as to resist oxidation.

'3rd. That when the iron is "coming to nature," the puddler washes this adhering film of sulphide and phosphide into the cinder, just as a laundress washes adhering greasy dirt from the solid fibres of linen, &c., into soapy or alkaline water, grease being diffusible in such water, as liquid sulphides and phosphides of iron are diffusible in the cinder. This diffusibility is proved by analysis of the cinder wherein the phosphides and sulphides are afterwards found, just as the dirt from the clothes is found in the soapy water that has been used by the laundress. The action of the squeezer, hammer, and rolls, in removing the still adhering portions of fusible cinder, is thus strictly analogous to the "wringing" of the laundress.

'Another analogy will further illustrate my meaning. Here is a specimen of crude paraffin-scale, as obtained by the distillation of cannel coal or bituminous shale. This, as you will see, is very different in appearance and physical properties from this refined paraffin. The crude scale is soiled and greasy. It leaves a dirty film upon the fingers,

while the refined paraffin is a beautiful, hard, pearly substance, that may be handled freely, and leaves no mark behind. Besides this, the melting-points of the crude scale and the refined paraffin differ considerably, the scale being fusible at a much lower temperature than the refined paraffin, just as pig-iron fuses at a lower temperature than finished iron.

'How, then, is this crude paraffin converted into refined paraffin?

'By a process curiously resembling puddling. It is fused in a bath of liquid hydro-carbon (like the liquid cinder-bath of the puddler), and is then allowed to cool. On doing so, "it comes to nature" like the iron—*i.e.*, granules of infusible paraffin separate gradually from the liquid paraffin oil. By agitation of these they are washed in the liquid, and the adhering and more fusible impurities are diffused through this liquid. The solid paraffin is now separated from the liquid by a straining process, like "balling up," and is then squeezed, just as the puddled balls are squeezed, only that the squeezing is done in bags, and under hydraulic presses, instead of steam-hammers and rolls. By this means the fusible impurities are removed, and this beautiful substance, now so largely used in the manufacture of candles, is produced. The more frequently it is thus washed and squeezed, the purer, harder, and less easily fusible it becomes, its value being tested by its melting-point and freedom from adhering greasiness or other impurities.

'I have been led to this rather simple theory by carefully watching the work of a good puddler, and learning as much as possible from his unlettered wisdom, which I profoundly respect, in spite of its crudity.

'In the first place, when the iron is first melted he

gropes about the bottom of the furnace with his rabble. Why? In order to promote oxidation. Scraping away the film of fettling that has been reduced by the carbon and silicon of the pig, he exposes a fresh surface of oxide that shall similarly become reduced, by giving up some or all of its oxygen to oxidise the carbon and silicon of the melted pig. Thus he promotes the boiling, and, when this is fairly started, the separation of granular iron commences. He now rabbles with increased energy, bringing fresh portions of melted pig in contact with the oxidising fettling, and washing the granules as they are formed, or "come to nature." The climax of his efforts is made when this coming to nature is maturing or about matured. If I am right, the reason for this is that, just when the granules are formed, and before they agglomerate into larger grains, the greatest surface is exposed to the washing action, and the efficiency of such washing is the greatest; and, therefore, his success depends largely upon violent agitation just at this stage of most effective washing.

'When the iron is "dry"—*i.e.*, deficient in silicon or silicates—he adds more hammer-slag or cinder in order to obtain a good "bath," and, the more liquid his cinder, the better results he expects to obtain. Additional cinder is to him what rinsing-water is to the laundress, and I have no doubt that, if it were practicable to re-wash the ball in fresh silicates quite free from sulphur and phosphorus, the iron would be improved in quality.

'I should add, that the bath of cinder serves another purpose—viz., that of protecting the spongy iron from oxidation; and, accordingly, the puddler, when he has balled up, and is waiting for the hammer—*i.e.*, while the first and second balls are being shingled—carefully covers the later balls with as much cinder as possible.'

This lecture was also reported in 'Iron,' vol. vii. p. 170, and was followed by a controversy on the subject between Mr. Nordenfelt and myself in the same volume of 'Iron,' March 4 and 11, 1876. The following is a copy of this correspondence:—

'*To the Editor of* "IRON."

'Sir,—In your paper of the 5th ult. is a summary of Mr. W. Mattieu Williams' lecture on the above-mentioned subject, in which the lecturer, after mentioning a suggestion of Dr. Percy, starts a new theory for the removal of the phosphorus contained in pig-iron by the process of puddling. While Dr. Percy supposes that a liquation, or sweating-out of the impurities takes place, Mr. W. Mattieu Williams considers that, while the removal of silicon and carbon is effected, as generally admitted, by an oxidising process, the phosphorus, on the other hand, is got rid of simply by the vigorous efforts of the puddler in rubbing and dashing the granules of iron against the liquid cinder, whereby the adhering and more soluble impurities are alleged to be washed off in a mechanical sort of way, without any oxidation. The lecturer further explained that, after silicon and carbon have been removed by oxidation, whereby the iron appears in a more infusible form, or "takes nature," the puddler, towards the end of the process, removes the phosphorus by the aforesaid rubbing, &c.

'In opposition to the suggestion of Dr. Percy, and still more to the theory offered by Mr. W. Mattieu Williams, it may interest your readers to know how this important question is looked upon in Sweden, where the chemical researches into the metallurgical phenomena have led to results which, generally, are satisfactorily confirmed by practical experience.

'If the lecturer is right in his theory, how is it to be explained that, the more raw the puddle-slag is kept, the less phosphorus is removed, although in this case the labour of the puddler is considerably augmented? Neither is any very considerable proportion of the phosphorus removed in hearth fineries, although a great amount of work is required in some of them, and in blowing Bessemer steel, as it is done in England, where the rubbing and dashing must be more effective than what can be produced by the strongest and most skilful puddler.

'In iron, as well as in steel, the phosphorus can only exist as a direct combination of phosphorus and metal without the agency of oxygen, whereas analyses of puddle cinders show that in cinders the phosphorus appears united with oxygen, thus forming phosphate of iron. If the purification were effected in the manner stated by the lecturer, how could the presence of oxygen be explained?

'In Sweden, it is considered fully proved that, if the phosphorus is at all to pass into the cinder, it can only be in the form of phosphate. The chemical affinity of phosphoric acid to oxidised iron in the cinder is, however, not stronger than that the phosphoric acid can again be easily reduced, especially at a great heat, through the combined influence of silicic acid, or raw slag, and the carbon contained in the fuel and pig-iron, in which case the phosphorus will immediately return to the metal, for which it has a great affinity.

'With these facts as a starting-point, it will be easily understood why the puddling process is capable of purifying the iron from phosphorus, while some other methods are almost ineffective in this respect.

'(1) *In the puddling* the slag is kept comparatively basic, and no fuel is there in contact with the metal.

The absence of carbon permits the oxidation of the phosphorus, and, as the basic slag contains a superfluity of oxidised iron, the phosphoric acid is able to enter the cinder as phosphate without interference from the silicic acid. In full accordance with this, the possibility of purification diminishes in proportion as the slag becomes more raw.

'(2) *In the hearth fineries*, although the cinder is kept very basic, the presence of carbon in the fuel, mixed up with iron, prevents the oxidation of the phosphorus, which thus remains in the metal, and does not join the cinder.

'(3) *In the Bessemer process*, in England, although no fuel is in contact with metal, the cinder, on the other hand, keeps so exceedingly raw through the influence of the ramming of the converter (in fact, so raw that no alienation of carbon and silicon could be effected but for the excessive heat and thorough mixture of the slag and the metal), that, even if the phosphoric acid were produced, in the absence of carbon, the oxidised iron in the cinder would be so surcharged with silicic acid that the phosphoric acid would have great difficulty in entering the cinder. The phosphorus would, in this case, be forced to return again into the metal.

'It should also be mentioned, that analyses of puddle-cinders, taken at different stages of the puddling process, have shown that the phosphorus is removed chiefly at the beginning of the process, and not when the iron "takes nature," as stated by the lecturer, depending upon the fact that the chemical affinity between the iron and the phosphorus is less strong at the commencement of the puddling, when the iron holds a considerable portion of silicon and carbon, than later on, when these ingredients have been removed. In some instances the analyses have actually shown that a part of the phosphorus, which may have

passed into the cinder at the beginning of the process, will return to the metal later on, when the iron has lost silicon and carbon, and thus become more attractive for the phosphorus than the cinder is.

'Yours, &c.,

'THORSTEN NORDENFELT.'

'*To the Editor of* "IRON."

'SIR,—In the last number of "Iron" are some critical remarks on my theory of puddling, by Mr. Thorsten Nordenfelt, to which I reply with much pleasure, as the objections are perfectly fair, are thoughtful and suggestive, besides representing the Swedish view of this subject.

'In the first place, Mr. Nordenfelt does not exactly understand me, probably from having merely read an abstract. I say that mere oxidation will not remove phosphorus, but I do not deny that it may be oxidised when removed, or in the course of removal, to the liquid cinder, which, I contend, separates it by a washing action similar to that by which the laundress removes greasy stains from linen, &c. The analogy is very close, the grease being saponified when it enters the basic suds, just as the phosphorus may be oxidised, and combine with the basic oxides of the puddler's cinder. The problem to be solved is, Why should the puddler, by the mechanical work of his rabble, do that which all have failed to effect by *mere* chemical action? (In the Henderson process, as I stated, the chemical action is supplemented by the mechanical agitation due to the violent effervescence, which is protracted beyond the ordinary boiling-stage, and continues after the granulation and separation of the iron is completed—*i.e.*, the work of the rabble is done by the escaping gas.)

'If oxidation and the mere presence of cinder effects the conversion of phosphorus into phosphoric acid, and its combination with oxide of iron, why does the open hearth, or "finery," fail to remove the phosphorus; and why, also, does the Bessemer process? In both cases there is abundant oxidation, abundance of cinder; and in the latter there is, also, abundant agitation, but it is not the same kind of agitation as that which I contend is the effective agency of the puddler—viz., *the agitation of solid granules of infusible iron, wetted by a small quantity of adhering and fusible phosphide of iron, in the midst of a liquid cinder capable of carrying away, either by combination or diffusion, or both together, this adhering liquid impurity.* In the Bessemer converter all is liquid together; there are no granules to be washed, the iron being quite as liquid as the cinder. Returning to the analogy of the laundress, I may say that she can wash dirty fibres by agitation in soapsuds, but cannot cleanse dirty water by the same means. Mr. Nordenfelt speaks of the "rubbing and dashing" of the Bessemer process. But this is not quite correct; there is plenty of dashing, but no "rubbing," in the sense that I use the word—that is, the rubbing of solid particles against a liquid.

'The statement in the last paragraph of Mr. Nordenfelt's letter, that "analyses of puddle-cinders taken at different stages of the puddling process have shown that the phosphorus is removed chiefly at the beginning of the process," is quite at variance with the results of my own investigations of this subject.

'An umpire is, therefore, needed, and for this purpose I will call in Bauermann, and quote from his "Metallurgy of Iron," page 310, where he says, that "The chemical changes involved in the process of puddling have been

investigated by Calvert and Johnson, Lan, Schilling, and Drassado, both in England, France, and Germany. The method followed by these chemists was similar in all cases. Samples of the iron and slag taken from the furnace at different times during the puddling were analysed, and the results tabulated." He then summarises the general result of these investigations by stating that "the removal of the foreign matters in combination with the iron takes place in the following order: first silicon, then manganese, then phosphorus, and lastly sulphur; the latter element being most difficultly removable. In the treatment of grey pig-iron, the graphitic carbon is transformed into the combined condition after the removal of the silicon, during the melting of the charge."

'This accords with the results of my experiments, excepting in reference to the sulphur, which I have found to be removed simultaneously with the phosphorus, and rather more easily. Bauermann has, apparently, forgotten to state when the carbon is removed. I may add, that its removal commences after its conversion from the graphitic to the combined state, and that, generally speaking, the order of removal is greatly influenced by the quantity of the substance present. Thus, the silicon is not *all* oxidised and removed before the oxidation of the manganese and carbon begins, but its quantity is greatly reduced. This small quantity clings so pertinaciously to the iron that the oxygen now attacks more readily the greater quantity of manganese or carbon. If the quantity of sulphur and phosphorus is very great, a certain proportion even of their excess may be removed very early. In an extreme case, their removal *might* commence even before that of the silicon, as would happen with an impure pyrites, where

sulphur would be driven off by mere roasting. We must never forget that the difficult problem which the puddler has solved, is that of removing the small, the last, and obstinately-adhering quantities of sulphur and phosphorus. The reduction of 10 or 20 per cent. of sulphur to $\frac{1}{2}$ per cent. is very easy—it may be done in an open finery; the reduction of the $1\frac{1}{2}$ per cent. of phosphorus in Cleveland pig to $\frac{1}{2}$ per cent. is also easy—it may be done by other means than puddling. But the dragging out of this last $\frac{1}{2}$ per cent., the bringing it from $\frac{1}{2}$ to $\frac{1}{4}$, from $\frac{1}{4}$ to $\frac{1}{6}$, from $\frac{1}{6}$ to $\frac{1}{8}$, from $\frac{1}{8}$ to $\frac{1}{10}$, from $\frac{1}{10}$ to $\frac{1}{15}$, from $\frac{1}{15}$ to $\frac{1}{20}$, from $\frac{1}{20}$ to $\frac{1}{40}$, from $\frac{1}{40}$ per cent. to a trace, and from a trace to none, is a problem of progressively increasing difficulty, the last two steps touching the climax of practical impossibility.

'This must always be taken into account in receiving the evidence afforded by the composition of cinder examined in the manner above stated. If the experiments are made upon a pig that is excessively rich in phosphorus, a large proportion will oxidise and run into the cinder by the mere act of melting, and be found by analysis in the first ladleful. To accept this as evidence would be to conclude that mere melting is more efficient than puddling, inasmuch as it is quite possible to find a pig rich enough in phosphorus to lose about half by this mere melting; the same may be said of sulphur, though all of this would not be found in the cinder.

'To test the efficiency of the different stages of puddling, it is necessary to select a pig containing only a moderate, or small, quantity of sulphur and phosphorus. I may venture to affirm that, if this is done, it will be shown that the puddling is most effective just at that stage when a good puddler works his rabble with the greatest energy—

i.e., when the iron is coming, and has come, to nature, and just before balling.

'There is another risk of error in these experiments. It is that of concluding that the percentage of phosphorus added to the cinder at each stage represents the quantity taken during that stage from the iron. In spite of the natural and obvious appearance of this conclusion, it is utterly fallacious, and I suspect that Mr. Nordenfelt, like many others, has been deceived by it. We must remember that, up to a certain stage in the puddling process (*i.e.*, the complete granulation, or "coming to nature"), the total quantity of cinder, or slag, *is progressively increasing*, and therefore the mere *percentage* of any of its constituents does not measure their absolute quantity. Then, if the total quantity of slag or cinder at the end of the puddling is ten times greater than when the melting is just completed, the *percentage* of phosphorus, &c., indicated by the analysis of the cinder in this first stage, must be divided by ten before it can be compared with that in the last, or the addition of an equal percentage at this latter stage would represent a removal of ten times the absolute quantity it showed in the first. This, added to the fact that we are continually drawing from smaller supplies, and contending with the continually-augmenting difficulty of removing the latter traces, gives to the quantity of phosphorus entering the cinder at the later stages a potential value vastly exceeding that which is expressed by its mere numerical proportions.

'If Mr. Nordenfelt, and others who share his opinions, will re-examine these experiments in the light which the above-stated considerations throw upon them, their inferences may possibly be modified.—I am, &c.,

'W. Mattieu Williams.'

I was rather surprised, after all this publication and correspondence, to find in the 'Engineer' of November 16, 1877, the following in reference to a recent patent by Mr. Lowthian Bell.

'No one ever thought of washing phosphorus out of pig-iron before Mr. Bell; at least, if he did so, he kept the fact to himself. The very phrase "washing out" is practically new, and admirably describes what takes place.'

I may add that, in my sketch of the manufacture of iron and steel written for Stanford's book, in 1875, the word '*washing*' was printed in italics. It is true that I did not use the 'very phrase, washing out,' and for good reason; there is no washing *out*, but a washing *off*—a removal of the adhering phosphide from the surface of each granule; no mere washing could take any *out* of the substance of the granules.

In this consists the essential difference between my theory of washing and Dr. Percy's theory of liquation. If such liquation occurs—which I by no means deny—it is a sort of exudation, or sweating-*out* of liquid matter from within the material of the solid iron itself.

As the term 'liquation' is not a familiar one, it may be well to explain more fully its meaning, which is best done by an example which I will quote from Dr. Percy's exhaustive treatise on the 'Metallurgy of Lead.'

He tells us, on page 91, that 'when lead and copper are melted together at or beyond the fusing-point of copper, and the molten metal, after having been well stirred, is put into an ingot-mould, and very quickly cooled, an apparently homogeneous product, or alloy, is obtained. If this alloy, or any other composed of lead or copper in relatively large proportions, similarly prepared, is kept

heated for a considerable time at, or somewhat beyond, the melting-point of lead, liquation will occur: lead containing copper will trickle down, and a more or less porous mass of copper containing lead will eventually be left.'

The granulation, or 'coming to nature,' of the iron in the puddling-furnace may be described as a sort of inverted liquation, the solid granules separating, or precipitating, from the more fusible liquid compound, instead of the liquid oozing from the solid. In the case of the copper alloy, the action starts in a solid, the liquid oozing therefrom; in the case of puddling, it starts in a liquid, the solid precipitating therefrom. If this did the work of purification, vigorous rubbing would be unnecessary, instead of being so specially effective and essential.

A certain degree of true liquation does, I suspect, occur at a later stage, and may co-operate in rendering the washing more efficient. This liquation, as it occurs in the separation of lead from copper, appears to be due to what, for want of a better expression, I may term a 'reticular' or net-like solidification of the less fusible metal, in the meshes or pores of which the more fusible is retained, and from which it is gradually squeezed out as the solidifying metal contracts.

Keeping in view these facts, and others connected with this action of liquation, I think that its aid in the purification of iron is more likely to be effective after the ball has left the puddling-furnace—*i.e.*, during the shingling, rolling, and re-heating, or what I have, in accordance with the washing-out analogy, called the 'rinsing' stages, when, as we all know, large quantities of fluid slag are beaten or squeezed out of the mass.

In reference to this, it must be remembered that if a puddled bar from which all this liquid has been apparently

squeezed is re-heated, a large additional quantity oozes from it. When a pile is being wheeled on a trolly from the re-heating furnace to the rolls, this fluid slag still runs freely from it, and more is exuded while it passes between the rolls. This may be true liquation.

The slag which is thus squeezed out under the hammer by the squeezer or the rolls, contains less sulphur and phosphorus than the cinder of the puddler's bath. The puddler has, somehow, learned this without the aid of the chemist, for, long before any comparative chemical analyses were made, he was in the habit of preferring this 'hammer-slag' to his own cinder when he required to add such material to his charge. He has also another motive in this selection: it is richer in metallic iron, as well as less weighted with his enemies, the sulphur and phosphorus.

Connected with this there is a curious fact in reference to the use of the words 'cinder' and 'slag.' Scholars who have devoted the best years of their life to the study of words and etymologies continually confound and misapply these words, while the old-fashioned puddler and mill foremen use them in scholarlike accordance with their etymology. 'Cinder' is derived from the German 'sintern,' to trickle, and is probably connected with the still older Scandinavian verb, 'sindra,' to throw out sparks, in which sense the word is used in the sagas of the old Norsemen, from whom we obtained our earliest instruction in metallurgy. The workman gives the name of 'cinder' to the fluid scoria which trickles from the furnace, or, in modern, large-scale workings, flows rather than trickles. That which is struck out by the blows of the hammer he calls 'slag.' The old Norse for a blow is 'sla' and 'slog;' the modern Norsk is 'slag,' the German, 'Schlag.'

The failure of rotatory puddling, or any other system

of mechanical puddling that merely agitates in the same manner throughout, is explained on the washing-out theory, which indicates the absolute necessity of intelligence in puddling—*i.e.*, of modifying the kind of agitation according to the stage of action that is reached. As the time required to reach any given stage varies so greatly with the quality of the pig and the condition of the furnace, no set rule for the adjustment of a machine can be followed. The most hopeful direction in which to apply mechanical puddling is that of constructing machines that will aid, rather than supersede, the muscles of the puddler.

It is evident from the above that the heat of a puddling-furnace should not be excessive—*i.e.*, not so great as to cause the granules of iron to be fused by solution in the cinder, as scraps of wrought iron are fused in the bath of a Siemens-Martin furnace. Even an approximation to this is damaging, as a near approach to fluidity (iron softens and melts gradually like sealing-wax) would cause the agitation to effect a remixing of the cinder and its impurities with the iron, rather than a washing-out of liquid from solid. Overheating has been proved to have this effect.

Before concluding this part of the subject, a very ingenious and scientific device of the illiterate puddler demands explanation.

As already stated, he supplies his fire with a maximum of oxygen during that part of the process in which oxidation is required. This he does by raising the chimney-top damper, and loosening the coal near the fire-hole; but, as soon as the granules are fully formed, he lowers his damper, to limit the draught of oxygen, thereby rendering his reverberatory flame neutral, and only hot enough to maintain the temperature, without raising it any further.

Finally, when the granulation is complete—*i.e.*, when the unoxidised silicon and carbon no longer exist in sufficient quantity to protect the iron from direct oxidation by their strong affinities for the oxygen—the puddler blocks the opening of his furnace fire with lumps of coal, which he stands on the little shelf in front provided for that purpose. He might have a nicely-hinged, well-fitting door, if he would ask for it; and I have heard 'superior' people speak sneeringly of the inherent coarseness of his vulgar nature being manifested by this preference of the clumsy coal lumps, when he might have a proper door.

In this case the superiority is all on the side of the puddler, his lump of coal being in reality an elegant and truly scientific device for attaining the necessary object—viz., a reducing flame instead of the previous neutral flame, and the first oxidising flame. The coal being thus placed, a little air enters all round each lump, but the inner face of each lump is heated to a glow by the radiation of the fire; thus, the air must strike the glowing face of coal as it eddies inwards, and in so doing its oxygen combines to form carbonic oxide. This carbonic oxide is the reducing agent required. If a close-fitting door were in the place of the coal, it would, when shut, exclude all air, and force the draught to find its way through the rabble-hole, where it would do serious mischief by 'cutting'—*i.e.*, burning the iron where its fresh oxygen must necessarily impinge. If he left the stoke-hole open, free oxygen would enter there.

CHAPTER VIII

HAMMERING, SQUEEZING, AND ROLLING

The Fibre of Iron

In order to work out the problem of the rationale of the treatment to which iron is subjected after it leaves the puddling-furnace, we must understand the condition of the ball which the puddler hands over to the shingler. A recapitulation of the changes that occur in the puddling-furnace will assist in making this clear.

A compound of iron with carbon, silicon, sulphur, phosphorus, &c., is melted, its fusibility depending upon its combination with these elements; pure iron being infusible in a puddling furnace. As the puddling proceeds, these elements are separated and oxidised, forming a still more fusible, vitreous compound—the 'bath' of 'cinder.'

In the midst of this liquid the infusible iron is precipitated in the form of small granules. But these granules, although not liquid, are by no means absolutely solid. They are viscous—*i.e.*, soft and plastic, like the end of an iron bar when heated to the same temperature in a blacksmith's fire. In this condition they may stick together like half-melted glass, or wax, or pitch, but, being harder than the resinous substances, demand more pressure to effect their cohesion.

This, I contend, is the whole philosophy of welding, which has been considerably mystified by far-fetched

explanations. Every other solid which melts gradually by passing through an intermediate viscous or softened condition is similarly weldable. Ice, when approaching its melting-point, is easily weldable, as every man who has been a boy, and has made a snowball, knows by practical experience of the different consistency of a snowball that he attempted to make when the thermometer stood far below the freezing-point, and one made when the ice-granules were beginning to thaw. This case of ice-welding has been even more mystified than that of iron by the introduction of the theory of 'regelation.'

The action of the puddler in 'gathering' the granules of iron from the midst of the liquid cinder may be correctly compared with the gathering of a snowball from a puddle of snow-broth, where granules of plastic or viscous ice are diffused in water. The puddler gathers the granules of iron to one end of his furnace, raising them a little above the pool of cinder, squeezing them, as he proceeds, to keep them together; and when he has accumulated a ball of the largest size he can lift, he picks it up, and deposits it on the lorry, to be hurried away, and placed under the hammer or in the squeezer.

Let us now observe what happens as the mass of aggregated granules is wheeled along, and placed upon the block of the steam-hammer. Yellow-hot liquid dribbles from the ball as it stands on the lorry, and oozes out while it lies on the block. This, upon examination, proves to be similar in composition to the pool of cinder from which the ball is gathered. It is, in fact, the cinder that still remained between the granules of iron. The first blow of the hammer, as it crushes down the soft, loosely-cohering, spongy mass, squeezes out more of this; and as the hammering proceeds, and the further welding of the particles

together gives greater compactness and more resisting power to the ball, the squeezing out continues; but that which now comes out (the slag, properly so called) is richer in iron than the cinder left behind in the furnace. The puddler learned this, and used it in preference to the cinder for fettling his furnace long before the chemist discovered the difference by comparative analysis.

The cause of this difference is not difficult to understand. Each granule of iron has been formed by the aggregation of material round an infusible nucleus. This is indicated theoretically, and also by the fact that, when the iron is 'coming to nature' in the course of puddling, the granules are at first very minute and far apart; they gradually grow, and form a kind of *purée*, or iron porridge, by their growth and approximation. It is evident that the primary nucleus must be composed of the most infusible material—*i.e.*, of the purest iron—and the superficial part of each full-grown granule of more fusible material. As the squeezing under the hammer proceeds, more and more of this outside film is pressed out, and thus the slag becomes richer and richer in iron.

This goes on until the mass is cooled down below the fusing-point of what remains of the outer coating of the granules. After this the hammering merely condenses the mass, and completes the welding of the granules together. The result is rough, puddled bar.

As every practical ironmaker knows, puddled bar is materially improved by re-heating and re-beating. The view of the constitution of the puddled iron above expounded renders this improvement clearly intelligible. The re-heating raises the temperature sufficiently to fuse the film of less pure, and therefore more fusible, iron which surrounds each granule, and the re-beating squeezes this out.

Careful observation will render this action evident. As the re-heated mass is brought from the re-heating furnace to the hammer, a quantity of liquid trickles out from it, and more is exuded as the hammering and rolling proceeds.

The trickling out is more strikingly shown when the puddled bar is cut into faggots, and piled; it still continues even after several re-heatings and intermediate rollings. The finest quality of wrought iron (as regards softness and toughness) is thus obtained by repeatedly re-heating and re-rolling, thereby squeezing out more and more of the inferior, outer skin of each granule, until little more than the original nucleus of pure iron remains. As already explained (*see* experiments on armour-plates at Sheffield, page 135), there is a limit beyond which this re-heating must not be carried, and this limit is determined by the removal of the residuum of the more fusible compounds of iron constituting the impurities enveloping the granules. Such fusible compounds, be they carbides, silicides, phosphides, or sulphides, protect the pure iron from oxidation; but, when they are gone, oxidation commences, not merely on the surface, but throughout the substance of the iron, when it is raised to a welding-point, or thereabouts. The specks of black oxide were plainly seen (and, if the samples were preserved untarnished, may still be seen) in the middle, and throughout the fracture of the thick armour-plates described on page 135.

Besides this expurgation of the more fusible impurities of the iron, there is another advantage obtained by re-heating as usually conducted in making the best qualities of iron. The puddled iron is rolled out, and sheared into faggots; these are piled, heated, and then welded together. This mixes up the different parts of the puddled iron, and

thus renders it more nearly homogeneous; not completely homogeneous, as we all know, but it effects a certain degree of approximation to this desirable quality.

The desirability of this intermingling is evident when we consider what has already been stated on page 133 concerning the difference of composition, as regards carbon, of the balls that are successively drawn from the same heat in a puddling-furnace. Although three of these may be to some extent squeezed into each other, and mixed up together, in the course of shingling them into one bar under the steam-hammer, there must be three qualities of iron therein, besides the differences existing in the same ball on account of the greater oxidation at its surface than its interior when exposed to the air on drawing it from the furnace.

I will now discuss the chief mystery of the structure of wrought iron—viz., its 'fibre.'

What is this fibre?

We know that organic substances, such as the muscles of animals and the stems of plants, have fibres, and that these fibres are definite organic structures, elongated cells, &c.; also, that there are certain minerals with fibrous structure, the fibres being usually composed of long, acicular, or needle-like crystals. But the metallic fibre of iron is something quite different from either of these.

How is it formed? Why should it be displayed in wrought iron, and not in cast iron or cast steel, nor in *castings* of the semi-steel or 'homogeneous iron,' now so largely used, nor in castings of any other metal or alloy?

A little further reflection on the constitution of the puddled ball, as above expounded, and on the treatment it receives after its first hammering, will, I think, evolve a respectable solution of this metallurgical problem.

When the mass of granules has been welded together by the hammer or squeezer, it is rolled, and thereby drawn out or elongated. Now, what thus happens to the whole of such a mass must also happen to all its constituent parts—*i.e.*, each of the granules will be elongated, each little grain will be drawn out as a fine wire or fibre.

If each granule were perfectly homogeneous, and were fused into perfect homogeneous union with its surrounding neighbours, these elongations would not be visible as distinct fibres; but if the above view of the nucleated constitution of each granule be correct, each must have just sufficient individuality and structure to be separately visible on fracture.

That this is the case we know by the distinct granular structure of puddled bar. This same puddled bar, when rolled much beyond its original length, becomes fibrous by the elongation of each of these individual granules. If this explanation be correct, the direction of the fibres should always be that of the elongation effected by rolling.

Every practical ironmaker knows that such is the case; and if he makes a fracture in order to display fibre, he always breaks the iron crosswise to the direction in which it passed through the rollers.

Another test, and a rather crucial one, may be applied to this theory—*i.e.*, by comparing the fibre of iron which has been *rolled* into wire, and thus elongated very greatly, with the fibre of iron of similar quality that has only been rolled moderately, as when rolled into plates or rails. The fibre of the wire should be finer than that of the plates or rails. Such I have always found to be the case, and others have, doubtless, observed the same.

I have observed something further—viz., that puddled bar which has been hammered only, not passed through

the rolls, has a scaly fracture, as though made up of minute flat plates or scales, the edges of which are seen in a fracture, as they lie one upon another. These I regard as the granules merely flattened, but not yet elongated.

If these views of the structure of wrought iron are correct, its tenacity, as tested by direct pull, should be greater in the direction of the length of a rolled plate than in that of its width.

It is well known that such is the case. In the official specifications of the tests demanded by the Admiralty this difference is definitely stated, the amount being based on the results of a very large number of carefully-made experiments. For first-class plate-iron the ratio demanded is 22 to 18; for second-class, 20 to 17—that is, strips 3 inches wide and $\frac{1}{3}$ inch thick (the usual standard), with their lengths in the direction of rolling, should bear a longitudinal pull of 22 and 20 tons respectively; but if pulled crosswise to the rolling, the test is reduced to 18 and 17.

It is evident that, in the first case, the break must occur by tearing the fibres themselves, but in the second it may be effected by a severance of fibres from each other—is, in fact, a test of the tenacity of the weld rather than of the fibre of the metal.

In applying a bending-test, this difference should be still more decided, as the cracks on the surface, when bending a long crosswise strip, may run all along the welding-joints of distinct fibres; while in bending one that is cut lengthwise the welding-joints are mere points dotted here and there at the irregularly-distributed ends of the fibres. The Admiralty allowance is, in this case, 125 degs. lengthwise to 90 degs. crosswise for first-class, 90 degs. lengthwise to 60 degs. crosswise second-class.

Turning to a report of the results of a large number of experiments made by Mr. Kirkaldy on so-called 'steel' plates (more properly, homogeneous cast iron) made by the Landore Siemens Company, I find that the mean result displays no practical difference between the behaviour of the plate whether tested lengthwise or crosswise. By skilful bending a sort of fibre may be displayed in this homogeneous iron, but critical examination proves the constituent crystalline granules of this cast metal to have been elongated merely by the bending. The difference between these granules and those of the puddled iron will be discussed when I come to the subject of the structure of cast steel.

In judging the quality of fibrous iron, something more than the mere coarseness or fineness, or the quality of the fibre, should be examined. The fibres should be of uniform structure and colour, which uniformity constitutes the silky character so much esteemed. If the enveloping fusible impurity of the original granules has not been sufficiently removed, it shows as a dark, dull skin upon each fibre, constituting a dirty or cottony, rather than a clear, silky fracture.

All theories demand criticism, and should be tested, whenever it is possible, by what Lord Bacon calls the '*experimentum crucis*.' This crucial test should be a special experiment—a novel one, if possible, which shall bring about a definite, predicable result, if the theory is sound—a result following as an evident consequence of the theoretical cause. Such an *experimentum crucis* may be tried in order to confirm or refute the theory of iron-fibre above expounded.

If such fibre is produced by rolling out and elongating the granules formed in puddling, a different structure

should be obtained by simply working a puddled ball without any rolling whatever—*i.e.*, by making *wrought* iron that shall not be *rolled* iron. This may easily be done by placing a small puddled ball under the hammer, beating it out into a circular, flat disc instead of a bar. Then let this disc be re-heated and re-hammered, so as to spread it out equally in all directions, and thus form a moderately thin, circular plate. Having done this without any rolling whatever, cut this hammered plate into strips, and bend and break them as in bending and breaking rolled iron, to show the fibre. The fracture of the purely hammered plate will prove to be scaly instead of fibrous. This will be best shown by taking a piece of good rolled plate of same size, cut lengthwise, bending and breaking in the same manner, and then carefully comparing the two.

Allowance must be made for the obvious fact that, in the act of bending, the scales or plates of the hammered iron will be strained and stretched—*i.e.*, drawn out somewhat—and thus the granules which have been beaten into nearly circular scales will become oblong scales or flattened fibres. A short fracture, with the least possible bending-stretch, will show the structure, by presenting the edges of scales instead of the ends of fibres, as in rolled iron. Etching with acid should reveal a difference of structure, but I have not yet tried this.

CHAPTER IX

WHAT IS STEEL?

THE following is from Gmelin's 'Handbook of Chemistry,' vol. v., page 207 (Cavendish Edition):—'According to Clouet, steel contains, on an average, 3·1 per cent. of carbon; according to Vauquelin, 0·71.' This shows how great are the discrepancies among high scientific authorities concerning the composition of steel. Further examples will be shown as I proceed.

The mere definitions of what is steel, and what is not, are similarly contradictory. Since the introduction of the Bessemer process such definition has become really difficult.

Before this, steel might have been defined as a compound of iron and carbon that could be hardened, softened, tempered, and welded. The welding fixes the superior limit of carbon. As already explained, carbon increases the fusibility of iron; and when its proportion amounts to about 2 per cent. and upwards, the fusion occurs so suddenly that there is no available intermediate condition of soft solidity, or what I may term waxiness, upon which, as I have already endeavoured to show, the weldability of iron and all other weldable substances depends. I say *about* 2 per cent., as the limit varies considerably. As phosphorus, sulphur, and silicon also increase the fusibility of iron, a small amount of these impurities lowers the

quantity of carbon which the iron will take without losing its weldability.

This superior limit of the definition of steel remains the same as of old; but when we come to the minimum, the modern methods of producing what is called steel render it impossible to draw a hard-and-fast line between iron and steel. Old-fashioned steel made by cementation rarely came down below $\frac{3}{4}$ per cent. of carbon. This would formerly have been regarded as very mild steel. Now we run down from this to so-called steel which contains as little as $\frac{2}{10}$ per cent. of carbon.

It has been proposed to draw the line by applying the name of steel to all that is cast in ingots, and limit that of iron to such as is only wrought by welding; but there is a serious objection to this, as it would exclude all the steels that are made by the old-fashioned method of cementation and shearing, without casting. One solution of the difficulty is that of applying the name 'homogeneous metal' to all the ingot material that is below the carbon standard usually demanded for steel rails—viz., $\frac{4}{10}$ per cent. This is quite low enough—rather too low from a mechanical point of view, according to which $\frac{5}{10}$, or $\frac{1}{2}$ per cent., might be taken; but this would not be commercially tolerated, as '*steel*' rails are in demand by those who know little or nothing of carbon percentages, and who would, therefore, suppose that they were not getting what they order unless the rails were described as 'steel' on the invoice.

The $\frac{1}{2}$ per cent., as the lower limit, about corresponds to what is demanded by the old definition of steel—viz., a compound differing from iron by its capability of being hardened, softened, and tempered. This property,

practically, though not absolutely, disappears when the proportion of carbon descends below 0·5 or 0·4 per cent.

I am by no means disposed to haggle over mere words and definitions, but there are cases where fallacious definitions have conveyed false ideas that have led to serious practical mischief.

This is strikingly exemplified in the definitions or descriptions of cast iron and steel which are still to be found in text-books on chemistry, where cast iron or pig-iron is described as a compound of iron and carbon, and steel as another compound of the same elements, but with less carbon; and the statement that wrought iron, being free from carbon, steel is simply an intermediate compound.

Formerly this was affirmed very definitely, even by the best of practical metallurgists; thus, in Mushet's 'Papers on Iron and Steel' (1840), page 526, is the following: 'It will appear evident from these and former experiments that crude iron and steel only differ from each other in the proportion of carbon they contain.' Dr. Percy ('Iron and Steel'), page 778, says:—'If steel be regarded simply as iron carburised in degrees intermediate between malleable and cast iron, then it is obvious that the latter, during its conversion into the former, in the processes of fining and puddling, must pass through the state of steel.' Gmelin ('Handbook of Chemistry,' Cavendish Edition, vol. v., page 210) says:—'Melted cast iron, whether white or grey, yields white cast iron by sudden cooling, and grey by slow cooling. The former corresponds to hardened, the latter to unhardened, steel, excepting that the steel contains less carbon.'

In Miller's 'Elements of Chemistry'—one of the best moderate-sized text-books in the English language—the subject of the 'Manufacture of Steel' commences thus:—

'Iron, when combined with a smaller proportion of carbon than is contained in cast iron, furnishes the valuable compound known as steel.' In an address delivered by Prof. G. F. Barker, of Yale College, before the American Institute, he says:—'Steel holds an intermediate place between cast iron and wrought iron. In the process of making wrought iron there has been made, at one time, steel, and if the process could be stopped in the right place, the whole would be steel.' A multitude of similar quotations might be made, all to the same effect.

If these descriptions are true, how very absurd is the ordinary Sheffield process of making steel, where the manufacturer first doubles the cost of the pig-iron by his puddling, re-heating, rolling, &c., in order to remove all the carbon; and, having done this, he expends twice as much more by returning half of this carbon in the cementing furnace, and then re-melting, or shearing and tilting the blistered steel. Why not stop the first decarburetting process in the right place, and thus make the steel directly, at a less cost than that of wrought iron? Such has been the reasoning of hundreds of readers of these descriptions of steel.

It has often been said that half-truths are more mischievous than unmitigated fallacies. Such is the case in this instance. If the above descriptions of the relations of steel to cast iron were entirely wrong, they could be demolished at once, and their fallacy would become visible with the aid of but little explanation. As it is, a satisfactory demolition of the error demands an historical examination of its origin.

In the olden times, when only the purest native oxides were used in the production of iron, when charcoal was the fuel and reducing agent, and only small quantities

were made at once, cast iron or crude iron was simply a compound of iron and carbon; it was, in fact, a very hard, unweldable steel. The above-quoted definitions were *then* correct, and the conversion of this into a softer and less fusible compound of iron and carbon was a very easy process. Nothing more was necessary than to keep it hot while exposed to the air in small quantities, or to effect oxidation by the aid of a blast, or to make a mixture of wrought and cast iron.

The renowned Damascus blades and other weapons of old were thus produced, and tool-steel of very fine quality is still made in the same manner in India, in China, in Styria, and other places where primitive workers carry on their inherited handicrafts with primitive material and appliances.

What is now commonly called the old method of steel-making—that is, the Sheffield cementation process—is really a purely modern method; while the so-called new processes, such as the Bessemer and Siemens-Martin, &c., are merely revivals of the old primitive principle of steel-making, carried out with such modifications as are demanded by the differences of modern material and the modern demand for large-scale production.

The roundabout cementation process is essentially English, and arose in consequence of the English demand created by Dud Dudley's application of impure pit-coal to iron-making as a substitute for wood-charcoal, and the simultaneous use of our impure clay-ironstones in the place of the purer ores of the ancient ironmasters.

Before examining the rationale of this and the other methods of steel-making, I must brush aside a few more fallacies concerning the nature or composition of steel. Old knives may still be found stamped with what was

supposed to be a super-excellent brand, viz., 'silver steel' —*i.e.*, steel containing, or supposed to contain, a small proportion of silver alloyed with it.

Faraday and Stodart, in 1822, communicated to the Royal Society the results of a rather elaborate series of experiments on alloying steel with silver, nickel, rhodium, platinum, iridium, osmium, palladium, &c., and arrived at the conclusion that very small proportions of these improved the quality of the steel; that 0·002 of silver gave an alloy harder than cast steel, 0·01 of nickel gave a very hard alloy, susceptible of fine polish. Subsequent practical experience has not confirmed the expectations of these eminent chemists. The alloy may have had the hardening effect described, but this affords no evidence of improvement in the quality of the steel.

The idea that whatever increases the hardness of steel improves its quality, is a remarkably widespread error, not confined to vulgar, illiterate persons, but shared with them by men of great scientific attainments, as is proved plainly enough by the language used in this celebrated communication to the Royal Society, where it was read without any of the Fellows pointing out the fallacy, although it is a fallacy of the highest possible magnitude, seeing that it states a direct inversion of the truth.[1]

The hardening of a given sample of steel by the addition of any foreign substance is an evidence of its deteriorating influence. This assertion may appear rather a bold one to some of my readers, and even startling to those who are not practical steel-makers. I make it, nevertheless, with full confidence, and believe it to be of great practical import.

[1] The first deliberate attempt to refute it was made by myself, in the paper which is reprinted in the next chapter.

It is true that there are certain special purposes which demand special steels of excessive hardness, and in some of these cases mere hardness may be the primary and predominating desideratum. An extreme example of this is to be found in the bits of Franklinite described on page 36, which are mounted on a handle, or pencil, and sold for a penny each and upwards, as substitutes for glaziers' diamonds. This compound of the oxides of iron, manganese, and zinc is much harder than any steel, properly so-called, and so extremely brittle that, if ground to an acute cutting-edge, and that edge applied to do any cutting-work, it breaks hopelessly.

This and similar minerals are also found in masses, and when fused, and more or less reduced, so as to contain less oxygen or no oxygen, have a more metallic and steely character. In this condition they are made into steels for sharpening knives. They serve this purpose well enough while they hold together, but if dropped on hard ground they usually break, being nearly as brittle as glass. The hardness and brittleness go together.

The chisels used for turning cast iron and similar purposes must be made of very hard material—in some cases it must be so hard that the addition of a little silicon, or phosphorus, or of zinc or other metal, may be desirable; but such a tool must be a thick, clumsy thing, with an edge ground to nearly a right angle. If brought to a more acute edge, it will notch in working, and if an attempt were made to grind such material to a very acute edge—such as a razor or surgeon's scalpel—it would chip or notch, even when pressed on the grindstone—could not be made to take such an edge at all.

After what has lately been done by Thomas and Gilchrist in the removal of phosphorus in the Bessemer

converter, it appears scarcely credible that, up to quite a recent period, eminent chemists have maintained that it improved the quality of steel. In vol. v. (page 214), of Gmelin's 'Chemistry' (Cavendish Edition), we are told that 'Schafhautl remarks that cast iron, bar-iron, and steel almost always contain more or less arsenic and phosphorus, which often greatly improve their quality. Thus, the celebrated Dannemora iron and English Low Moor iron owe their good qualities to the presence of arsenic; and a particular kind of iron (marked CCND), from Demidoff's works, at Nischnetagilisk, is indebted for its peculiar qualities to the phosphorus it contains.'

As recently as 1869, when the 'Heaton process' of direct steel-making (by pouring melted pig on nitrate of soda) excited much attention and controversy, Dr. Miller reported that 0·298 per cent. of phosphorus in steel 'is obviously not such as to injure the quality'; and in a paper read at the Chemical Society, Dr. Paul confirmed this. He found 0·24 per cent. in samples of Heaton steel which was supposed to be of good quality.

They were good for such purposes as some of those above named, and their tenacity was very great. Brande stated that phosphorus improves the quality of steel, and founded this upon the fact, or supposition, that dies used for coining are improved by the presence of a little phosphorus in the steel.

Some fifteen or twenty years ago Mr. Riley showed to the Chemical Society a tool said to be improved by the addition of silicon. It was one of those heavy roughing-chisels above-described. He exhibited at the Society of Arts another tool made of such silicon-steel. It was a 'jumper'—*i.e.*, the heavy bar with a rude bevel used for boring rocks for blasting. Had he tried to make a fine,

acute-edged cutting-tool of any kind with such steel, I have no doubt whatever that it would have proved a failure.

The British Association has recently appointed a committee for investigating the influence of silicon on the properties of steel, and two reports have been submitted, which contain elaborate details of experiments and the usual tables of results of chemical analyses: rolling-tests, welding-tests, limit of elasticity tests, breaking load tests, 'ratio of limit to break,' extension, reduction of area, 'work done per cubic inch,' and hardness; but the report concludes as follows:—'It is to be regretted that, largely on account of the outlay it would have involved, these experiments have been conducted on a comparatively small scale, the ingots weighing only about 40 lbs. On this account *it has not been found practicable to perform tests connected with the resistance to shock, a point to which the attention of the Committee has been several times directed, and which is, from a practical point of view, of considerable interest.*'

The italics are mine, and the object of such emphasis will be understood by what follows.

In the second half of 1889 another outbreak of the silicon-steel epidemic occurred; its symptoms may be studied by reference to vol. xxxiv. of 'Iron,' where the customary tables of tensile strain, extension, and reduction of area may be found. Nothing is easier than the manufacture of *papers* on this subject, but the manufacture of keen-edged tools from the steel therein described is a very different problem.

As such silicon-steel can be made at a very little cost, and our steel-makers are not asleep, Mr. Riley's demonstration at the Chemical Society, above-referred to, would,

long ere this, have yielded important practical fruit had there been no mistake.

I venture to add a few words to warn my readers against a chemical fallacy that is freely expounded in these recent papers on silicon-steel. We are told that 'silicon will expel carbon, if the iron when melted contains all the carbon that it can hold, and a portion of silicon be added.' This addition, according to the experiments described, is made in the form of 'ferro-silicon'—*i.e.*, iron largely charged with silicon.

I do not question the stated results of these experiments, but venture to affirm that, if they were repeated with all the conditions exactly the same, excepting the addition of silicon, a similar loss of combined carbon would be discovered. If the steel were melted freely, at a high temperature, some of its carbon would be oxidised; if barely melted, at a lower temperature, much of the combined carbon would separate as graphitic carbon, without the aid of additional silicon. I have seen such separation displayed on a large scale in the cupola furnaces in which pig-iron is melted for Bessemer work.

Very pretty museum specimens of 'kish' (the glistening scales of separated graphite) may be thus obtained.

My own experiments on what may be termed 'pseudo-steels'—*i.e.*, iron combined with something else as a substitute for the carbon of true steel—indicate that phosphorus has about three times the hardening effect of carbon; thus, a sample of pseudo-steel containing $\frac{3}{10}$ per cent. of phosphorus is about as hard as true steel containing $\frac{2}{10}$ of carbon; that silicon has a hardening effect about intermediate—*i.e.*, $\frac{3}{10}$ of silicon is about equivalent to four-and-a-half tenths of carbon. I say 'about,' because such estimates can only be approximate, partly on account

of the difficulty of obtaining such compounds free from other impurities, and partly from the roughness of the available tests for hardness.

Reference to chemical text-books and technological treatises of different dates supply a number of curious and instructive examples of the prevalence of the fallacy of estimating the value of steel by its hardness.

A little reflection will show that the ordinary duties of steel demand a special ability to endure smart blows or vibratory shocks; the teeth of a saw or file, the edges of chisels, planing-irons, knives, and other edge tools, are continually receiving such shocks, and are ripped or notched unless they combine their hardness with remarkable toughness.

The same kind of endurance is demanded of steel used in construction. Why did the Tay Bridge give way just as the train came upon it? Was it merely the additional weight of the train? or was it chiefly due to the vibration produced by the train acting at the moment of extreme tensile strain produced by the wind on that fatal, stormy night.

In spite of all that has been said by high authorities concerning the improvement of steel by the addition of silver, platinum, chromium, palladium, titanium, tungsten, rhodium, silicon, manganese, &c., I maintain that, for general tool-making, and for every purpose where tenacity has to be combined with stability, and hardness with toughness, *the best material at present known is made by combining the purest of iron with the purest of carbon, and excluding everything else.*

Much has been claimed for nitrogen, and with much plausibility, seeing that certain nitrogenous organic compounds do assist in cementation; but my own opinion is, that the nitrogen in these does not act by combining with

the iron, but as a carrier of carbon in the form of cyanogen or its compounds. This will be further discussed when I reach the subject of cementation.

We may have alloys of iron with other metals of great value for certain purposes, and I believe that a wide field is open for further research in this direction; but it is not only clerically inaccurate to give the name of steel to such alloys, but is practically misleading and mischievous.

My own experiments indicate that what I have above described as true steel—*i.e.*, iron and carbon practically free from other constituents—is not only tougher in proportion to its hardness than any other metallic substance at present known, but it has what I will venture to describe *as a greater range of temperability.*

By this I mean that the difference between its greatest hardness and its least hardness, or greatest softness, is greater than that of any of the pseudo-steels. A pseudo-steel of iron and phosphorus, or iron and silicon, may be annealed, hardened, and tempered to some extent; but the range of difference is very small compared with what I call true steel, composed of iron and carbon, and, practically, nothing else.

The practical importance of such wide range will be understood at once by reflecting on the fact that the value of steel as the material for tools, &c., depends upon its being capable of acquiring such modified hardness that it may be made to cut, forge, and otherwise shape itself.

CHAPTER X

FALLACIES CONCERNING STEEL

THIS chapter, which is supplementary to the preceding, is a reprint of the first of a series of 'Papers on Iron and Steel' which I contributed to 'Nature' (vols. ii., iii., and iv., 1870 and 1871). In Chapter IX. there is, necessarily, some repetition of the *beginning* of this paper, which is fully justified by the fact that, although twenty years have elapsed since I first pointed out these fallacies, the supply of their victims has not yet ceased, as reference to the specifications published by the Great Seal Office will show.

'A friend of mine has been converting some common cinder pig-iron into either very fine iron or steel, by a very simple process, but does not know who to apply to to learn its value. He is willing to share the profit with any one who will help him in the matter. I have some small samples of it, if you would like to see it, or can tell me who would be likely to interest themselves in the matter. From what I can make out, I should think it would make good steel, for it will harden and temper now.'

The above, quoted from a letter I recently received, is a typical sample of a number of others I have had at different times, and it represents the labours of quite a multitude of patient, long-suffering, and miserably-deluded investigators. The published specifications of abandoned

patents make painful record of wasted time, money, and ingenuity, and suggest dark tragedies of ruined hopes, all arising from the same misunderstanding of the changes which take place in the conversion of ordinary pig-iron or cast iron into *merchantable* steel.

The most humiliating feature of this delusion is that it is not the offspring of popular ignorance, is not prevalent among the beer-drinking class of ironworkers who sign their names with a ×, but crops out among intelligent, self-taught men, who have studied the chemistry of iron and steel as expounded in recognised chemical books. The costly fallacy I allude to is directly traceable to the teaching of our highest scientific authorities.

By reference to almost any text-book on chemistry, it will be found that cast iron is described as a compound or mixture of iron and carbon; that steel is another compound or mixture of iron and carbon, but with a less proportion of carbon; and that wrought iron is nearly free from carbon. Further, we are told that the ordinary method of making steel is, first to remove all the carbon from the cast or pig-iron by making it into wrought or bar-iron, and that this bar-iron is afterwards converted into steel by causing it to take up a new dose of carbon in the cementing furnace.

The natural inference of a thinking reader is, that this is a clumsy complication, especially if he knows that the process of cementation is slow and costly—that, on account of the irregular diffusion of the carbon in the blistered bars, other expensive processes of shearing, tilting, casting, &c., have to follow. Why not at once produce the steel from the cast iron by a process of decarburisation which shall stop at the right point—*i.e.*, when the 3 or 4 per cent of carbon of the cast iron is reduced to the 1 or 1½ per

cent. required to produce steel? By doing this, not only the cost of converting wrought iron to steel, but also the cost of puddling to produce wrought iron, will be saved; and steel, which is but a carburet of iron intermediate between cast iron and wrought iron, instead of being so much dearer than either, could be made at an intermediate cost, or cheaper than wrought iron.

If he dips further into the literature of the subject, and reads the history of the manufacture of iron, he will find fresh confirmation of such reasoning, as he will learn thereby that the direct production of steel is an ancient art, and that weapons of renowned quality were made from steel thus produced.

By reference to one of the most recent and elaborate English treatises on the subject—Dr. Percy's 'Metallurgy'—he will find, on page 778, that this is described as 'the ancient method, which is still extensively practised on the Continent, especially in Styria;' and, further down on the same page, that 'if steel be regarded simply as iron carburised in degrees intermediate between malleable and cast iron, then it is obvious that the latter, during its conversion to the former, in the processes of fining and puddling must pass through the state of steel.' On page 805 of the same work he will find further confirmation of his theory in the words, 'it is obvious that steel must be produced by melting malleable iron and cast iron together is suitable proportions.'

I might multiply quotations from this and every other work I have seen in which the chemistry of iron and steel is treated, and show by each of them that the thousand-and-one of unfortunate inventors who have struggled in vain to make steel from English pig-iron, have been en-

couraged in their delusion by the teaching of high chemical authorities.

If steel be regarded simply as 'iron carburised in degrees intermediate between malleable and cast iron,' these inventors are perfectly justified in seeking some substance which, at the melting-heat of cast iron, will give off a definite quantity of oxygen; and they have logical grounds for believing that, by bringing such a substance in contact with the molten cast iron, and properly regulating its quantity, they may burn out just that surplus carbon which makes all the stated difference between cast iron and steel.

As a multitude of compounds when thus heated do give off oxygen, a vast field of effort is open, and, accordingly, every available peroxide and decomposable oxygen salt has been administered by strange devices to the melted iron; the same obvious substances used over and over again, and the same failures continually repeated by expectant inventors, ignorant of what others have done or are doing. Gas and vapours have been blown over the surface and under the surface, and through, from bottom to top, of melted cast iron, and all (including Mr. Bessemer) have failed to produce merchantable steel from ordinary English pig-iron, without making it, first, into malleable or wrought iron.

The reason of this is, that the removal of the surplus carbon is only a small portion of the work that has to be done in order to convert cast iron into steel of any commercial value. Several other substances have to be removed also, *and no process has yet been discovered by which these impurities can be removed, without at the same time removing the carbon in corresponding degree.* I put this in italics because I am convinced by experience of its

great practical importance; because I do not find it clearly and distinctly enunciated in any general or special treatise; and, further, because I have seen so plainly that the want of clearly understanding it is the rock upon which so many unfortunate inventors have split.

These inventors have not been informed, with anything like the necessary degree of distinctness, that the Styrians and others who have made, or are making, steel directly from cast iron, have started with a very different material to that which bears the name of cast iron in England, the difference being sufficiently great to totally change the conditions of the problem.

The cast iron of the Styrian steel-makers is a nearly pure, carburised iron; *our* cast iron is a carburised, silicised, phosphurised, and sulphurised iron. *Their* problem in steel-making is merely the partial decarburisation of their cast iron; *ours* is the practically complete desilicisation, dephosphurisation, and desulphurisation, in addition to this. Now, the partial removal of carbon from iron is one of the very easiest problems in practical metallurgy, while the complete removal of silicon, phosphorus, or sulphur, is among the most difficult.

To illustrate the grossness of the fallacy which represents the difference between cast iron and steel as merely, or 'essentially' due to carbon, I may state that, on looking down a tabular statement of the analyses I have recently made of thirty brands of ordinary English pig-iron (excluding hematite pigs), I find that seven among them contain less than 2 per cent. of carbon, or an average of 1·77 per cent. Now this is below the percentage of carbon which exists in some of the finest and most expensive samples of cast steel. Therefore, to convert these particular brands of cast iron into the finest steel, the

carbon must be neither increased or diminished; and if, as Dr. Percy says, the differences between steel, wrought iron, and cast iron '*essentially* depend upon differences in the proportion of carbon,' all these brands of pig-iron should be described as steel rather than cast iron.

Nevertheless, they are utterly worthless for any of the purposes for which steel is used, and the common result of the costly experiments of the inventors who endeavour to make steel directly from English pig-iron, is to produce a material very much like them.

They usually succeed perfectly in their effort to partially decarburise the pig-iron. They take away, say, one-half of the carbon, and with it a considerable portion of the silicon, and *some* of the phosphorus, sulphur, and manganese; but to make a *perfect* steel they must take away all of these latter, and leave nothing but pure iron and carbon. Absolute perfection is not, of course, practically attainable in steel-making, but it is approximated in exactly the same degree as the purification of the iron from everything except the carbon is effected.

The most notable modern attempt to produce steel directly by the simple decarburisation of English cast iron was that of Mr. Bessemer. His first idea was to blow air through the melted cast iron, and thereby to oxidise the carbon; and then, when a sufficient degree of decarburisation was effected, to stop blowing. He supposed that when by this means the proportion of carbon was reduced to about 1½ per cent., the result would be useful steel. He failed entirely in this; he never succeeded in producing merchantable steel from ordinary English cast iron by this method.

The Bessemer process, as at present conducted, consists in first oxidising, simultaneously, all or nearly all the carbon

and silicon, and then adding to the decarburised iron a new dose of carbon, by means of a known quantity of spiegeleisen of known composition—thus reverting to the old Sheffield principle of first bringing the cast iron to the state of wrought or decarburised iron, and then adding carbon to convert it into steel.

It is commonly represented that the failure of the early attempts at direct steel-making by the Bessemer process arose simply from the difficulty of determining the right moment at which to stop the blow, and thereby to regulate the proportion of carbon; and that the whole advantage of the spiegeleisen is the means it affords of doing this.

Dr. Percy says: 'In attempting to produce steel by the methods specified by Bessemer, it has hitherto been found very difficult, if not impracticable, *at least in this country*, to ascertain with certainty when decarburisation has proceeded to the right extent, and when, therefore, the blast should be stopped. Accordingly, the plan now adopted is to decarburise perfectly, or nearly so, and then add a given proportion of carbon in the state in which it exists in molten spiegeleisen, the precise composition of which should, of course, be known' ('Metallurgy'—'Iron and Steel,' p. 814). The italics are my own.

Neither in Dr. Percy's nor any other account of the Bessemer process do I find that the necessity of complete decarburisation as a means of completely separating the silicon is fairly appreciated.

If merchantable steel could be made from English pig-iron by simply stopping the blow before complete decarburisation, Mr. Bessemer would surely have produced *some* good steel in the course of his long and costly efforts which preceded the idea of introducing the spiegeleisen; for it must be remembered that the quantity of carbon required

in steel extends over a wide range—that steel may contain from 0·40 to 2 per cent. of carbon—and that steel with every degree of carburisation between this wide range is in demand in the market at good prices, provided it is free from phosphorus, silicon, &c. Nothing is practically easier than to stop the blow at such a moment as shall ensure a degree of carburisation somewhere within this wide range, and there can be no doubt that, in his early experiments, Mr. Bessemer, like other inventors of direct processes, made an abundance of iron that was duly carburised within the above-stated limits, although he failed to produce useful steel.

Dr. Percy's qualification, 'at least in this country,' is rather curious. He has, probably, learned that steel has been directly made in Sweden (though he does not mention it in his work) by the Bessemer process, and he seems to attribute this to the superior ability of the Swedish operators, enabling them 'to ascertain with certainty when decarburisation has proceeded to the right extent.'

I differ entirely from Dr. Percy in this conclusion, being convinced that Mr. George Brown, the manager of the Bessemer Department at the Atlas Works, Sheffield, who was the first to work the Bessemer process with commercial success, is better able (on account of his much greater experience and thorough knowledge of the work) than any Swedish manufacturer to determine when any required degree of decarburisation has been attained.

It is not the superior skill of the Swedish operators that has enabled them to make steel directly by the Bessemer process, but that they, like the Styrian workers, used a very superior charcoal-iron to start with; and that the blowing out of all the carbon was not absolutely

necessary for the sufficient purification of this quality of iron.

The greatest enemy to steel is phosphorus; $\frac{1}{10}$ per cent. is sufficient to produce serious deterioration, and even to render the harder varieties of steel utterly worthless. As our common English pig-iron is made from clay-iron-stones, many of the nodules of which contain, as nuclei or otherwise, the remains of fishes and other animal matter, they are exceptionally rich in phosphorus, and thus all the difficulties of steel-making are greatly increased in this country. There are few results in connection with the progress of British industry of which we have better reason to be proud than our pre-eminence as steel-makers, in spite of the greatest natural disadvantages; and this is more remarkable from the fact that so great a triumph has been gained by illiterate men, who have achieved it by following out with remarkably sound, though unaided sagacity, the strict method of true Baconian inductive investigation.

Whenever I meet a formulating, book-stuffed pedant, I love to tell him of the great, unconsidered fact, that while learned men of the Middle Ages were muddling their intellects with worthless disputations, the artisans of that period were true inductive philosophers, and that the revival of science only commenced when the men of the universities adopted the method which had always been followed by the men of the workshop.

If the men of the universities have outstripped the men of the workshop in recent times, it is simply due to the fact that science has kept systematic records of its achievements, by means of which each worker has the full benefit of the labours of his predecessors and fellow-workers, and is able to start from the point where these

left off; whereas the workshop observers and experimentalists have worked with little or no systematic co-operation.

If such co-operation only among one set of investigators has done so much, what may we not expect when it shall not only be extended to the other, but when both sections shall co-operate with each other? This technical and scientific co-operation is the great want of the present age. The artisan needs scientific education, and the professors of science have much to learn from the great mass of facts included in the practical experience of the workshop.

But I must not at present be further carried away into this tempting digression, but return to my main subject by anticipating an objection which will probably be made. The manufacture of puddled steel may be supposed to refute all I have said respecting the impracticability of producing steel directly from English pig-iron. If steel fit for the manufacture of files, chisels, &c., could be made from *ordinary* English pig-iron by this process, all my statements certainly would be refuted, for puddled steel is simply made by checking the oxidation, and arresting it at such a point that some of the carbon in the pig-iron shall remain unburnt.

The facts connected with the manufacture of puddled steel which bear upon the present subject are as follows:— First, puddled steel of merchantable quality cannot be made at all from *common* English pig-iron. Second, the manufacture of puddled steel has been much more successful on the Continent than in England. Third, only *mild* steel, and that of an inferior quality, is made by this process from English iron.

Referring to the first fact, I may mention that there is a great deal of mystery, and there have been a great

many failures, and much waste of labour, fuel, and iron in carrying out this process in England. In many forges where it has been tried, it is now altogether abandoned; and where it is carried on with any degree of success, there is usually much secrecy maintained.

The mystery is not in the puddling, as the necessary modifications in the supply of cinder and the working of the damper are well understood, and have been sufficiently explained in the specifications of abandoned patents and otherwise. The secret part of this process is the selection of the pig-iron, or, rather, the 'blend' of pig-irons, for it is found that a mixture of certain brands of pig-iron is better than any single brand used alone.

My own experience in connection with this subject has been very interesting, and is, I think, worthy of record. When engaged as chemist in the works of Sir John Brown & Co., of Sheffield, I made careful analyses of all the numerous brands of pig-iron that were used for various purposes in these works. These I tabulated, and kept continually before me, in order to compare their composition with the special uses to which they were applied, and the properties which they or the material made from them exhibited. The manager of the iron-department was a remarkable example of one of those self-taught, unconscious Baconian philosophers I have before alluded to. He had, during many years, been observing, experimenting, and generalising, his inductions consisting of a code of original rules for the manufacture of iron suitable for various purposes. Like the man who had talked prose all his life without knowing it, Jevons had been following strictly the injunctions of the 'Novum Organon' in discovering the best 'blends' of pig-iron for manufacturing respectively armour-plates, rails, boiler-plates, angle-irons, &c., and

among his other mysteries were certain blends for making puddled steel. These he called his 'steel-irons.' He selected these, like all the others, without having, or pretending to have, any knowledge of their chemical composition.

By quite a different path—*i.e.*, upon purely theoretical, chemical grounds—I had determined that certain brands among those I had analysed were the best fitted for making puddled steel, and was anxious to verify my theory. To have asked directly for a revelation of the iron-manager's secrets would have been unreasonable, and therefore I simply gave him a statement of the analyses of these particular brands, all arranged together, and called them 'steel-irons,' adding that, for the best work, I supposed that he mixed with them a proportion of a certain foreign brand. 'Hush! don't talk so loud; I don't want these fellows to hear you. Who told you that I used these?' was the substance of Mr. Jevons's reply. My theoretical and his practical selection proved to be exactly the same in result. He had selected just those particular pigs which contained the smallest percentage of phosphorus, and which, relatively to their carbon, contained the smallest proportion of silicon.

But this was not all. I had just concluded a number of experiments made for the express purpose of determining the function of manganese in the manufacture of iron and steel, and had come to the conclusion that its usefulness depends upon its readily oxidising, even before all the carbon is oxidised, and thereby affording a base with which the silica could unite and form a liquid and readily-fusible silicate. Now this is just what is wanted in making puddled steel, and hence I suggested the addition of the highly manganiferous foreign ore. He had recently

discovered that it did just what I expected that it would do, and supposed that his discovery was quite new. Such, however, was not the case, for this, like many other trade mysteries, had been independently discovered by a number of other practical investigators.

The foreign manganiferous metal referred to is spiegeleisen. Dr. Percy says:—'Spiegeleisen has been found admirably suited for the production of puddled steel of the best quality, and, accordingly, it is largely used for this purpose.' Now, spiegeleisen is remarkably free from those impurities which, as I have stated, cannot be removed from common English pig-iron without also taking out the carbon. I find that the average proportion of silicon to carbon in English pig is about three-fourths; in spiegeleisen it is below one-fourth: and that the average proportion of phosphorus in the samples of spiegeleisen which I have analysed is less than one-twentieth of the quantity contained in our Cleveland pigs. Three, four, and five hundredths per cent. is the quantity I ordinarily find in good German or Swedish spiegeleisen. The sulphur seldom exceeds $\frac{1}{10}$ per cent., and the large quantity of manganese materially assists in the removal of the silicon. It is, in fact, very similar to the Styrian cast iron, which, as I have already said, does not present the English difficulty of making steel by the direct process. Both are charcoal-irons made from remarkably rich and pure ores. The manufacture of cast iron from such ores, and steel from such cast iron, is mere child's-play compared with our native manufacture.

In reference to the second fact, that the manufacture of puddled steel has been carried out more successfully on the Continent than in England, I need only say that this confirms my statements, as the puddlers there are less

skilful than ours, and their raw material is a vastly superior charcoal-iron, such as I have already described.

The third fact—viz., that only *mild* steel of inferior quality is made by this process—is a further confirmation of what I have said respecting the necessity of removing the carbon from common pig-iron in order to purify it sufficiently to produce good steel; for, even with all this skilful selection of the purest pigs, and the mixture of spiegel-eisen with them, it is found in this country impracticable to make puddled steel containing more than ½ per cent. of carbon. Such steel is only fit for rails, tyres, for rubbish cutlery, and other purposes where a soft steel, or, rather, steely iron is used. If the puddling were stopped when the carbon was only reduced to about 1·75, or, say, 1·5 per cent. (the quantity contained in the best hard, cast steel), the puddled steel would be utterly rotten, it would crush under the hammer, whether hot or cold—the reason of this being that, even with the best English pigs, the selected 'steel-irons,' there would, with this amount of carbon, still remain a ruinous proportion of silicon, phosphorus, &c. It is necessary, with all available advantages, to bring down the carbon to within ½ per cent. in order to produce a workable material. Even then it is worth only about one-third of the price of good cast steel.

I might illustrate this subject still further by entering into the details of the chemistry of the Bessemer process and of Bessemer steel, by the history of the nitrate of soda process, and of other attempts to manufacture steel directly from cast iron; but I think the above is sufficient to expose the fundamental fallacy upon which all such attempts have been founded. I hope to have succeeded more particularly in demonstrating the very great error of those who, in their attempts to make such steel, have, like the

friend of my correspondent, whose letter opens this paper, deliberately chosen cinder-pig or other inferior iron upon which to make their demonstrative experiments.

This was the case with the Heaton Company. They worked for a long time, at Langley Mill, with one of the worst classes of pig-iron they could have selected for their purposes. I pointed this out to them in a letter printed in the 'Chemical News' of February 19, 1869. Heaton's effort, the most promising of all such attempts, on account of the action of the residual alkaline soda, was, through this serious mistake, never fairly tested. I witnessed some of their experiments, and analysed and otherwise tested the results.

There can be little doubt that, with properly-selected pigs, a material similar to puddled or Bessemer steel may be made by this process, and by several others that have been tried and have failed; but, with the common classes of English pig-irons, all such attempts to make steel directly by the partial oxidation of the carbon must of necessity fail, unless some entirely new, some hitherto utterly unknown method of removing the silicon, phosphorus, and sulphur of the pig-iron is also used. In such a case the novelty, the invention, the triumph, would consist, not in the decarburisation of the cast iron, but in the separation of the other ingredients.

I therefore recommend all inventors who seek to simplify or otherwise improve the manufacture of steel, to direct their attention, first, to the removal of phosphorus; next, to the removal of silicon; thirdly, to the removal of sulphur; and last, and least of all, to mere decarburisation, for that is a problem of the utmost simplicity, and already sufficiently understood.

CHAPTER XI

HARDENING AND TEMPERING OF STEEL

In many books, both popular and severely scientific, the term 'tempering,' as applied to steel, is used with nearly an opposite meaning to that which is accepted in the workshop. As an example—one selected from among many—I quote the following from an excellent and widely-circulated treatise, 'Ganot's Physics,' translated by Dr. Atkinson. We are there told that, 'by sudden cooling after they have been raised to a high temperature, many bodies acquire great hardness. This operation is called *tempering*. All cutting-instruments are made of tempered steel.'

In the workshop this process is called '*hardening*,' and the term tempering is only applied to the opposite process—the re-heating of the steel, by which the excessive hardness acquired by the first heating and sudden cooling is modified or tempered to suit particular requirements. In this sense the term 'tempering' describes a process of modified annealing or limited softening. Here the nomenclature of the workshop is, unquestionably, the more logical and truly scientific.

A cherry-red is the usual temperature to which steel is heated for hardening; but this is modified according to the quality of the steel or according to the amount of carbon it contains. High carbon cast steel is the least heated.

The methods of heating are various: simply, in a coal fire; in a flame, as the blowpipe flame; pinching in red-hot tongs; packing in an iron box with charcoal, and slowly raising to red heat; immersion in red-hot, melted lead: and other devices are used. In most cases, the object is to obtain a regular, equal temperature throughout, and the steel is accordingly 'soaked,' or left for some time exposed to the source of heat.

This, however, is not always the case, as some tools—such as broaches—are hardened only superficially, by immersing them for a very short time in a red-hot lead bath, and then rapidly quenching. The object of this is to obtain a soft core, and thereby increase the toughness of the body of the tool. Simple as it may appear, much skill and judgment is necessary in effectively heating, especially when the tools are of large size.

The cooling, or quenching, requires still more skilful management, as the contraction that would take place in slow cooling is checked in proportion to its suddenness, and the consequent hardening of the steel. If a long tool of any kind were cooled by dipping it sidewise into water, it would be curved by the unequal rate of cooling of the opposite sides. Thus, broaches, files, and all such tools, should be plunged perpendicularly. If the tool is unequally thick, the thick part should be dipped first, or cooled by some other device than dipping, as the equal immersion of the whole would cause the thin portion to be cooled throughout sooner than the thick part. Splitting, cracking, or bending might result from this, besides inequality of hardness.

Many small and thin tools are cooled by pinching with cold tongs, or between flat plates of metal, thus keeping them straight by mechanical force, as well as by equal

cooling. Small drills and similar tools are frequently hardened by simple heating with a blowpipe flame, and plunging the point of the tool into the tallow of the candle used as the source of heat. Melted tallow, oils of various kinds, mercury, brine, acids, soapsuds, and mysterious messes, are also used for quenching. In this, as in most things, there is much quackery, especially concerning secret hardening fluids.

In a lecture delivered at the last meeting of the British Association, Professor Roberts Austen quoted some curious old recipes for the liquids to be used in hardening steel, such as:—'Take snayles and first draw water of a red die of which water being taken on the first two months of harvest when it raynes; boil it with snayles; then take your iron red-hot, and quench it therein, and it shall be hard as steel.' Another recommends 'the blood of a man XXX. years of age, and of a sanguine complexion, being of a merrie nature and pleasant.' The workman is further told that, if 'he takes the juice of water of common beans, and quenches iron or steel in it, it will be soft as lead.'

I have seen many modern recipes, and read several specifications of patents for hardening fluids, all of about the same value as the snail-broth of earlier date.

Cast steel hardens with more equality and less distortion than shear steel, on account of its greater homogeneity. The unequal expansion due to unequal hardening is sometimes ingeniously used as a means of modifying the shape of steel articles. This inequality may be obtained by covering with clay the portion required to be the softest.

The distortion is due to the fact that, when a piece of steel is hardened, it becomes larger in bulk than when it was soft; and this increase of bulk is proportionate to the

hardening. Thus, if a straight rod of steel be made red-hot, then laid horizontally on water, and only partially immersed, it will become curved, with its convexity on the side more rapidly cooled. A steel plate similarly treated becomes 'dished' to some extent. If a soft, steel, cylindrical plug be fitted accurately into a hole or socket, it will not enter after hardening; its length will also have increased, as may be shown by careful gauging.

According to Elsner, the specific gravity of hardened cast steel is 7·6578; the same not hardened, 7·9288.

Steel thus hardened by simply heating and suddenly cooling is too hard and brittle for most purposes. It therefore requires 'tempering,' or 'letting down,' which is effected by re-heating in different degrees, according to the amount of softening demanded, which varies with the purpose for which the steel is to be used.

Such tools as files, roughing-tools for cast iron, jumpers, &c., are seldom tempered at all at their working parts, but are tempered or annealed in other parts, to prevent breaking. Thus, files are tempered at and near the 'tang.'

The higher the heat of the re-heating, the softer the temper. The workman has discovered an easy means of measuring the heat he applies for this purpose. Without reading Newton's 'Optics,' he avails himself of the beautiful property of colouration of thin films, which Newton investigated and expounded. These films are due to incipient oxidation, and vary in colour with the heat producing them.

Another method of regulating the temperature is to smear the tool with tallow, and watch the effect of the heat upon it; and another is to immerse the tool in a bath of metal or alloy that fuses at the heat required. An alloy

of lead and tin may be used thus. The following is a scale of tempers:—

	Colour	Temperature	Alloy	Effect on tallow
1	Pale straw .	420° F.	7 lead, 4 tin	Vaporises.
2	Straw . . .	450°	8 „ 4 „	Smokes.
3	Straw yellow .	480°	8½ „ 4 „	More smoke.
4	Nut-brown .	500°	14 „ 4 „	Dense smoke.
5	Purple . . .	530°	19 „ 4 „	Black smoke.
6	Bright blue .	580°	48 „ 4 „	Flashes if light is applied.
7	Deep blue . .	590°	50 „ 2 „	Continuous burning.
8	Blackish blue	640°	All lead or boiling linseed oil.	All burns away.

The first degree is the temper required for tools used in cutting iron (excepting the most obtuse chisels, which are commonly left hard), and for lancets and some other surgical instruments.

2 and 3, for drills, turning-tools for brass, and most of the tools used by watchmakers, mathematical instrument-makers, &c.

3, for penknives, razors, and tools of this class.

4, for scissors, stonemason's chisels, and the strongest of carpenter's and other tools for cutting wood.

6, for swords, cutlasses, bayonets, axes, &c.

7, for watch-springs, needles, fine saws (such as used for cutting brass), and other tools &c., in which elasticity is required. This is commonly called 'spring temper.'

8, common wood-saws and other tools roughly used for soft material. This is the lowest temper in ordinary use.

The above figures are those which I gave in my sixth Cantor Lecture, delivered February 21, 1876. They were based on the best information then obtainable, and still

may stand as fairly representing average results in the ordinary course of working.

A very interesting paper was read before the Birmingham Philosophical Society, June 18, 1889, by Mr. Thomas Turner, Lecturer on Metallurgy, Mason College, Birmingham, on 'The Colours produced during the Tempering of Steel.' It will be found printed *in extenso* in 'Iron,' January 24, 1890, and I take the liberty of quoting freely from it. Mr. Turner says:—

'I have frequently heated bright strips of polished steel for hours under the surface of mercury or oil without discolouration, while they would have been instantly coloured at the temperature used if heated in contact with air. I think, further, that there can be little doubt that the oxide so produced is practically transparent—first, because the sequence of colours is what would be expected in films of a transparent substance when the thickness of the films gradually increases; also because of observations on the reflected light, the colour of which varies somewhat at different angles; but chiefly because it is found that, on increasing the temperature a little above the point necessary to produce a dark blue, the colour gradually disappears (though, doubtless, oxidation proceeds more rapidly), and the surface, though covered with more oxide, becomes almost colourless again. When it is granted that the colours we are considering are the result of oxidation, it would at once appear probable that the nature of the surface to be heated, its freedom from dirt and grease, and the length of time during which it is heated, would all exert a considerable influence on the shade produced. It would also appear probable that the amount of carbon present in the metal, and the condition in which the carbon existed, would have com-

paratively little influence. Hitherto my experiments have been chiefly directed to the study of these simple, and, as they appear, almost self-evident conclusions.

'Heating has usually been performed in a large air-oven, inside of which, about 2 inches from the bottom, was an iron tray, supported on fire-bricks, and filled with sand to the depth of about 1 inch, a small space being left all round the tray so as to prevent contact with the sides of the oven. Resting on the surface of the sand, but not touching the edges of the tray, was a plate of copper, on which were placed the strips of steel it was desired to heat. The object of this arrangement was to prevent irregular heating from below, and to give as much uniformity as possible. Passing through the centre of the copper plate, and partly covered by the sand, was the thermometer used; and, as even with these precautions it was not found possible to get perfect uniformity, a considerable number of strips was operated upon at one time, and about four removed, from different parts of the plate, when an observation was made. I am indebted to Messrs. Perry & Co. (late Sir Josiah Mason) for specimens of bright crucible pen-steel, both in the soft and in the hardened condition, while Mr. G. H. Strick, of Brynamman, kindly supplied me with samples of bright wrought iron. It is, of course, necessary that for such experiments the steel to be used should be clean and bright. A rough surface does not give nearly the same brilliancy of colour as is noticed when the metal is carefully polished, though the shade is pretty nearly the same in both cases. The presence of dirt usually causes irregular colouring, producing bands or spots of colour different to the rest of the surface. Naturally, too, some kinds of dirt appear to assist oxidation, though the shade is less brilliant, while

other kinds of dirt exert a protective influence. The brightest shades are produced with perfectly clean and polished surfaces, and few people are aware of the gorgeousness of the shades of purple and blue which can be produced on a large surface with proper conditions.

'In connection with the supposed relationship between colour and temper, I have taken strips of bright steel, hardened and unhardened, and also bright wrought iron, and heated them as above described, at various temperatures, for definite periods, and find that, practically, each of these three varieties of iron gives the same colours in the same time. The only difference I have been able to perceive is that the hardened steel gives the brightest colour, and the wrought iron the least brilliant. This difference in brilliancy is, no doubt, due to the fact that the surface was more perfect in the hardened steel specimens, which had been carefully cleaned by rotation with sand in barrels for a lengthened period. The fact that in each of the three classes the shade produced under similar circumstances is identical, shows at once that the colour on a steel tool is no indication whatever as to the contents of carbon or the temper of the steel. As bearing on this aspect of the question, it may be mentioned that Bousfield patented (1866, No. 2810) a method of blueing the surface of sheet-iron. After the sheets had been properly cleansed, they were heated in an airtight flask for a good many hours at 700 degs. Fahr., care being taken that no two sheets were in contact with each other. Probably a lower temperature, and a shorter time, with free access of air, would produce a similar result. I notice, too, that in some cases cast iron is coloured in a similar manner, and this fact confirms the above conclusions.

'From the very beginning of my experiments I have

been struck with the fact that *time* has a most important influence in developing these colours. From a study of ordinary text-books one might readily conclude that to produce a light straw colour about 221 degs. C. (462 degs. Fahr.) is necessary, while about 320 degs. C. (648 degs. Fahr.) is required to produce a blue colour. Such a conclusion would, however, be quite erroneous, for it is easy, by heating the specimens for a comparatively lengthened period, to produce a blue colour at a temperature below that which is usually regarded as necessary to give a straw colour, or over 100 degs. below that which is generally accepted as producing a blue. In the same way, a straw colour can be produced, in a few minutes, fully 50 degs. below 221 degs. C. (462 degs. Fahr.), which is the generally-accepted temperature. It will be found, however, that as we pass from shade to shade up the series, each colour requires a longer interval for its production at a given temperature than the one which preceded it. Thus, at a given temperature, we may pass from very light straw to straw—a well-marked change—in a few minutes, while at the same temperature it may require almost as many hours to pass from purple to blue. Further, in starting with low temperatures, the intervals of time between the various shades are greater, and become very considerable indeed for the deeper shades. For example, a purple can be produced at 250 degs. C. (514 degs. Fahr.), in a few minutes, which would require an hour at 220 degs. C. (460 degs. Fahr.), or about twelve hours at 170 degs. C., though the ultimate result would be the same in each case.

'On the other hand, it can be shown that, with a deficiency of oxygen, iron or steel may be heated far above the temperatures previously mentioned without producing

the usual succession of colours. Thus, in annealing sheet-iron in the manufacture of tin-plates, a number of sheets are heated to redness for some hours in an iron box, from which the air is excluded as far as possible. On removing the sheets when cold, they are found to be straw-coloured or brown in the centre over perhaps two-thirds of their area. Surrounding this centre portion, passing outwards in order, are found purple, blue, light blue, blue-green, and nearly colourless, depending on the amount of oxidation, though the sheets themselves have been exposed for a considerable time to a red heat. Bousfield's patent, above mentioned, is another example of the same kind. Details of a few of my own experiments, undertaken to try and determine the interval between definite shades, may serve to illustrate these facts. Thus:—

Total time of heating at 221°–227° C.	Interval between samples	Colour
5 min.	—	Dark straw.
12 min.	7 min.	Brown.
21 min.	9 min.	Brown, with purple.
32 min.	11 min.	Nearly all purple.
45 min.	13 min.	Purple, with some blue spots.
60 min.	15 min.	Very similar.
77 min.	17 min.	Nearly all blue.
95 min.	19 min.	Very similar.
117 min.	21 min.	Deep blue.
140 min.	23 min.	Blue, with slight tinge of green.

'Several of the above colours are "bastards"—*i.e.*, transition colours, and, although the last interval (twenty-three minutes) is more than four times as long as the first (seven minutes), still the early intervals are too long, and the later ones too short. Another experiment gave—

Total time of heating at 220°-227° C.	Interval between samples	Colour
1 min.	—	Very light straw.
4 min.	3 min.	Light straw.
9 min.	5 min.	Straw.
16 min.	7 min.	Brown.
25 min.	9 min.	Brown, with purple.
36 min.	11 min.	Brown and purple about equal.
49 min.	13 min.	Purple, with some brown.
64 min.	15 min.	Purple, with blue.
81 min.	17 min.	Nearly all blue.
100 min.	19 min.	Blue.

'In this experiment, though the time of heating varied as the squares of the numbers from 1 to 10, still the intervals were too short in the later samples, and transition colours were obtained. The earlier samples, also, were not so definite as might be desired, though it would be difficult to express the slight variations in words. The following was a more successful experiment:—

Total time of heating at 220°-227° C.	Interval between samples	Colour
2 min.	—	Very light straw.
4 min.	2 min.	Straw.
8 min.	4 min.	Dark straw.
16 min.	8 min.	Brown.
32 min.	16 min.	Brown, with purple.
64 min.	32 min.	Purple.
128 min.	64 min.	Dark blue.
256 min.	128 min.	Greenish-blue.

'The last of the three experiments gave far the best results, as judged by the distinctness of the shades produced. Hence, at the temperature used (220 degs. to 227 degs. C. (460 degs. to 473 degs. Fahr.) corresponding closely with 221 degs. C., commonly accepted as giving a straw colour), the time required to pass from one distinct shade or colour to the next increases approximately in

geometrical progression. Dr. Poynting has suggested that at the temperatures used in my experiments the film of oxide first formed may act as a protection to the surface of the metal, and that the rate at which the thickness of the film increases may be represented by a logarithmic curve. I do not venture to suggest that a similar rule would hold good for all temperatures—of that I have no evidence; but this is certain, that at low temperatures, such as, say, 150 degs. C., the various colours can be produced, but it requires very prolonged heating in order to obtain the blue shades. On the other hand, the lighter colours can be produced at a high temperature, but require very little time for their development. I have not attempted to determine the lowest temperature at which these colours can be produced, and should imagine it would be difficult to do so accurately. I have, however, succeeded very well at 150 degs. to 160 degs. C. (302 degs. to 320 degs. Fahr.), and do not doubt that with sufficient time a still lower temperature would suffice.

'Though the foregoing observations prove that the colour developed is dependent as much upon time as upon temperature, and that the colour is independent alike of the amount and the condition of the carbon present, so long as the surfaces and other conditions are alike, still these observations merely suggest another and more important question—namely, how far the temper of the steel may be affected, and its properties changed, by continued heating at a temperature below that which is generally employed for tempering. Hitherto I have not been able to obtain quantitative results in this connection, owing to the fact that steel strips, even when carefully hardened, not only differ in the various pieces, though cut off the same sheet and treated in the same manner, but

even the same strip will very commonly differ in hardness on the two sides, and not infrequently, even in a strip of only some 3 inches in length, one side of the strip will be different at each end, while the middle will not agree with either. Hence some more satisfactory method of experiment is required. But in the meantime I have satisfied myself that hardened steel strips, if heated for some hours at 220 degs. C. (460 degs. Fahr.), are distinctly softer than similar strips which have been heated for a shorter time; and that though a few minutes at 220 degs. C. produces a distinct effect, the interval has to be considerably increased from time to time in order to produce further and further appreciable softening of the steel. I am informed that the experience of steel-pen manufacturers lends support to the above opinions, and I may venture, in conclusion, to refer to other observations in the same direction. Brande ("Chemistry," 1848, vol. i., p. 759) gives the following interesting details in reference to the preparation of knife-edges for a pendulum used by Captain Kater ("Phil. Transactions," 1818, p. 38), the details of which preparation were not given in Captain Kater's original paper. Brande states that the knife-edges "were forged by Mr. Stodart from a piece of fine wootz; they were carefully hardened and tempered in the bath at 430 degs. Fahr.; on trial they were found too soft. They were a second time hardened, and then heated to 212 degs. The intention was to increase the heat from that point, trying the temper at the advance of about every 10 degs. In the present instance this was not necessary, the heat of boiling water proving to be the exact point at which the knife-edges were admirably tempered." "It is highly probable," Brande continues, "that steel for many uses may be sufficiently tempered in a range so extensive as from 212 degs. to

430 degs. Fahr. (100 degs. to 221 degs. C.). But it is not the temperature only, but also the time during which the steel is exposed to it, which influences its hardness or temper." As confirming the view that steel may be tempered at a lower temperature than is usually supposed, there are also the experiments of Professor Langley ("Proc. Inst. M.E.," 1882, p. 148), who showed that the density of steel was distinctly reduced (*i.e.*, the steel was hardened) by cooling rapidly from the boiling-point of an alkaline solution used for removing the scale from the specimens examined. So far as my observations have gone I believe—

'1. In the words of Brande:—"It is not the temperature only, but also the time during which the steel is exposed to it, which influences its hardness or temper."

'2. High carbon-steels are more sensitive to the effects of comparatively low temperatures than are steels containing less carbon.

'3. The colours observed in tempering steel can be produced by suitably varying the conditions, at temperatures either far above or below those usually accepted as necessary to produce a particular shade. The colours can be produced alike with hardened or with unhardened steel, and with wrought iron or cast iron, as well as with steel. They are, therefore, independent of the amount or condition of the carbon present in the steel.'

The above facts clearly show the practical importance of time in the operation of tempering; but we have still to learn *what are the equivalents of time and temperature.* By this expression I mean, How much longer must a given low temperature be maintained in order to produce the softening effect of a given higher temperature? We require to learn, for example, how long must, say, 400 degs. Fahr., be

maintained in order to produce the same degree of softening as 500 degs. maintained one minute.

Mr. Turner's experiments show how much more time is demanded to obtain *the differences of colour*; but the practical question is, whether a given colour, say nut-brown, if obtained by heating at 500 degs. Fahr. for two minutes, will indicate the same degree of softening as when obtained by heating to 460 degs. in sixteen minutes, as in Mr. Turner's experiments.

This is difficult to determine, on account of the want of any well-defined measure of hardness. It is very curious if the colouring and softening go together—*i.e.*, if the increase of time demanded for passing from straw to blue (or any other interval) should produce the same degree of softening as the rise of temperature demanded for effecting the same change of colour; or, otherwise stated, if superficial oxidation and softening throughout are correspondingly affected both by time and temperature. I suspect that this really is the case, within very narrow limits of error. My reason for this is, that experience based, not merely on a few laboratory experiments, but upon countless millions of workshop experiments, has proved that we may rely on colour only, although such colour is practically obtained through most varying degrees of time.

I will take as an example the common mode of tempering, which I have myself applied a few hundreds of times, in my apprentice days, between 1834 and 1841, to such, tools as drills, turning-tools, gravers, punches, &c. This method was simply to lay the tool upon an old file made red-hot, and watch the colour, then plunge the tool into water immediately. In these cases the time required varied very greatly—from less than one minute up to five

or ten minutes, according to the thickness of the tool and the temperature of the old file. In spite of this, I never found that a little drill, which acquired its straw colour in a few seconds (whether heated thus or in a candle-flame), was perceptibly harder than a roughing lathe-chisel that was ten times as long in heating.

I should add that Mr. Turner's results, as regards the effect of time in producing the colours, are confirmed by workshop experience, which tells us that the colouring proceeds, to some extent, even after the heat is withdrawn. If the tool laid upon the red-hot old file is raised to, say, a pale straw, then withdrawn, and laid on a wooden bench to cool slowly, it will deepen to a full straw, or from purple to blue, and so on. This change varies with the bulk of the tool, and its consequent time of cooling. Hence the general practice of plunging the tool in water immediately it is "let down" to the required tint.

CHAPTER XII

PHOSPHORUS IN STEEL

The Nature of its Mischievous Action

PRACTICAL iron and steel makers have long, and certainly, known that phosphorus is damaging to both iron and steel; but beyond the general fact that it produces 'cold shortness,' the nature of the mischief is still so imperfectly understood that I think it desirable to devote a chapter to its further elucidation.

More than twenty years have elapsed since I first expounded my views on the subject, and these views having been disputed, rather superciliously, by well-recognised scientific authorities, the fairest as well as the clearest way of treating the subject is to reprint the controversy as it stood, with such comments as subsequent progress demands.

'PHOSPHORUS IN IRON AND STEEL.

'*To the Editor of the* "CHEMICAL NEWS."

'Sir,—In the "Chemical News" of January 29, page 58, is an abstract of a paper by Dr. B. H. Paul, read at the Chemical Society, on "The Connection between the Mechanical Properties of Malleable Iron and Steel and the Amount of Phosphorus they Contain," and a report of the discussion which followed it. Judging from these, it

appears that the very serious fallacy upon which Dr. Paul's conclusions were based was not detected by any of the distinguished chemists who were present and took part in the discussion.

'The fallacy I refer to is that of judging of the quality of steel by Mr. Kirkaldy's tests of tensile strain, &c. Had Dr. Paul carried his researches further, by examining in the same manner the relative tenacity of several samples of iron (or of steel containing but little carbon) which varied only in the quantity of phosphorus they contained, he would, probably, come to a much stronger conclusion, and have asserted, as some Continental chemists have done, that phosphorus up to 0·50 per cent. improves the quality of steel. The action of phosphorus on iron and steel is to increase their hardness and their brittleness when cold, and at the same time—within certain limits—it increases their tenacity, provided they are not already highly charged with other hardening constituents. I refer here only to the tenacity as measured by a *direct and gradually-applied longitudinal or axial strain.*

'If the iron or steel were required for tie-rods, to be subject only to a strictly axial pull that should never occur suddenly, and that should be quite unaccompanied by vibrations, Dr. Paul's conclusions that 0·24 per cent. of phosphorus would be quite a harmless quantity, and Dr. Miller's statement that 0·298 per cent. of phosphorus in steel-iron "is obviously not such as to injure the quality," would be quite correct, for steel-iron for such a purpose would be improved by that amount of phosphorus. It is, however, quite obvious that such a combination of conditions is practically impossible.

'When we consider the work to be done by the edge of a chisel, a hatchet, a sword, a graver, or a turning-tool;

by the teeth of a file or a saw; or the duty of edged tools generally, it is obvious that the power of resisting a sudden, a vibratory, and a transverse shock is the property most demanded. Now this is just the property which phosphorus tends to destroy. An excess of combined carbon has a similar effect, and it is impossible to obtain hardness without a sacrifice of toughness; but this sacrifice is much greater when hardening is obtained by phosphorus than when it is conferred in an equal degree by carbon.

'I have never tried the experiment, but have very little doubt that a factitious steel might be made in which phosphorus should replace (in a lower proportion) the carbon of ordinary steel, and that such a factitious steel would take a very respectable position if tried by Mr. Kirkaldy's direct tensile test *only*. It would, however, be practically useless, on account of its incurable brittleness. This brittleness would be indicated by Mr. Kirkaldy's *extension test*, but not to its full practical value, on account of the gradual application of the strain and the absence of vibration.

'Phosphorus has another prejudicial effect upon steel, which is not in the slightest degree indicated by either the tenacity or the extension tests. I refer to the intractability of the hardness which it confers. The hardness which carbon gives to steel possesses the characteristic and invaluable susceptibility of annealing and tempering; it may, within certain limits, be modified through an infinite series of gradations, and the steel thereby may be worked by steel, and adapted to the multifarious uses for which it is required. The hardness conferred by phosphorus is, practically, a constant quantity at a given temperature. It disappears when the iron or steel is heated, and returns on cooling; but, as far as I have at present

been able to learn, the rate of cooling does not sensibly modify it.

'I make the above remarks with all due deference to Dr. Miller and the other eminent chemists whose opinions on this subject I have ventured to controvert; but as my daily work is amidst the volcanic belchings of Bessemer converters, the thumping, crashing, and earthquaking of steam-hammers, &c., I have opportunities of comparing the results of chemical analysis with the verdicts of practical trials which are quite unattainable in any college laboratory. With all these advantages, I find the solution of such questions as the action of small quantities of phosphorus so very difficult, that I make the above remarks, with some diffidence, as a crude exposition of approximate knowledge.

'As regards the Heaton process, which has led to this discussion, I may state that I have visited Langley Mill, and examined the work done there, on behalf of the company by whom I am employed; and although it is not my intention to here express any opinion as to the general merits or demerits of the process, I cannot refrain from saying that it appears to me that Mr. Heaton is somewhat misled on this particular subject of phosphorus—that he is not doing justice to himself in making his early trials chiefly with inferior pigs containing excessive quantities of phosphorus. Had he directed his first efforts to the production of the best quality of steel from the best quality of pigs, rather than endeavouring to compete with the Bessemer process in the race of cheapness, I believe that his results would have been more satisfactory and conclusive.

'The difference in value between the best and the worst qualities of British pig-iron is about 3*l.* per ton;

while the difference in value between the best qualities of cast steel and an ordinary Bessemer steel rail is quite ten times that amount; and I suspect that the conversion of the best pigs to steel of a given hardness would be effected with a smaller quantity of nitrate than is required for those of inferior quality. The worst sample of Heaton steel that I have analysed contains 0·24 per cent. of phosphorus; the best, only 0·05 per cent. They differ widely in other respects. The first sample I saw made was from an inferior pig-iron from the neighbourhood of Mr. Heaton's works which I had already analysed; the second was, I believe, made from a pig of very superior quality to this. The difference in value between the two products is many times greater than that between the raw materials.

'W. MATTIEU WILLIAMS.

'The Laboratory, Sir John Brown & Co., Sheffield:
'*February* 13, 1869.'

This letter was published in 'The Chemical News,' February 19, 1869, and elicited the following reply from Dr. Paul (February 26, p. 106):—

'I will take this opportunity of mentioning that the fallacy which your correspondent, Mr. Williams, ascribes to me, in reference to this subject, exists only in his imagination.

'No opinion was offered by me as to the quality of the steel, and my communication was restricted to pointing out the fact that steel of considerable tensile resistance contained an amount of phosphorus much larger than had previously been observed to exist in steel of good quality.

'According to the statement of Mr. Williams, he would appear to be master of an amount of knowledge,

and opportunity of judging respecting this subject, which do not fall to the lot of most chemists, therefore it might, perhaps, be regarded as presumption on my part to endeavour to justify myself in regard to the tensile strength of steel, as a character which the presence of phosphorus would be the most likely to affect, provided the commonly-received opinion as to the influence of that substance on steel be correct. For this reason, I will not venture to offer any reply to Mr. Williams's letter, but merely express my hope that, in his next communication, he may, from the abundance of his resources, confer upon chemists the benefit of something more of fact, and less opinion.—I am, &c., 'BENJAMIN H. PAUL.

'8, Gray's Inn Square:
'*February* 24, 1869.'

To this I replied as follows (March 5, page 117):—

'*To the Editor of the* "CHEMICAL NEWS."

'SIR,—I am sorry to see that Dr. Paul, in replying to my letter on the above subject, has merely perpetrated a few commonplace sarcasms, which cannot throw any light upon the chemical relations of phosphorus to iron, and which were certainly not called for by any remarks of mine.

'That the fallacy I referred to does exist somewhere outside of my imagination can be seen at once by reference to the "Chemical News" of Jan. 29 (p. 58). Anybody who refers to that Report,[1] the accuracy of which Dr. Paul does not question, will see that he commences with the statement that "it is generally considered that very small quantities of phosphorus in malleable iron and

[1] This Report is reprinted *in extenso* in the Appendix to this Chapter.

steel are most prejudicial to the quality of the metal," and that "quite recently an eminent metallurgist has stated, as a fact, that much less that 0·3 per cent. of phosphorus produces a decided and injurious effect upon steel." He then proceeds to controvert that statement, and bases his controversion on the fact that "he had recently had an opportunity of testing the truth of this conclusion by determining the phosphorus in some samples of iron and steel," &c. He then states *how* the quality of these seven bars of iron and two bars of steel was tested—viz., by Mr. Kirkaldy's tensile strain and extension tests; he gives Mr. Kirkaldy's figures, and those of his own analyses, and, finding that the iron and steel containing so much phosphorus stood these mechanical tests so satisfactorily, he "*therefore* thinks himself justified in asserting that the commonly-received opinion on this subject does not always represent the truth."

'The object of my letter was to show that this reliance upon the gradually-applied tenacity and extension tests is fallacious; that these tests, though of great practical value in determining some points, do not detect the special mischief which phosphorus, in small quantities, does to iron and steel. It was quite evident, from the discussion which followed the reading of Dr. Paul's paper in the Chemical Society, and from expressions of opinion recently made in other places, that Dr. Paul is not the only one who has been misled by the application of these tests, which, as I explained, may even represent all kinds of malleable iron, and some kinds of steel, as actually improved by the addition of a little phosphorus, on account of the increased tenacity of a peculiar kind which it confers.

'When I referred to my own position as chemist to

one of the largest and most important ironworks in Europe, it was not, as Dr. Paul insinuates, with the view of self-exaltation, but to indicate that, in pointing out a mistake made by him and Dr. Miller, I was merely correcting a technical error which any chemist not having such daily and special "opportunities of comparing the results of chemical analysis with the verdicts of practical trials" would be liable to make.

'I confined myself to a general statement of the facts (Dr. Paul seems to regard brittleness, tenacity, hardness, cold-shortness, &c., as only "opinions") best known concerning the special characters of the deterioration produced by phosphorus, simply because my letter had already made a sufficient demand both upon your columns and my time; but if the subject is considered sufficiently interesting, I shall be happy to take an early opportunity of supplying you with some illustrations of the special instances from which the general inductions are derived.—I am, &c.,

'W. MATTIEU WILLIAMS.

'The Laboratory, Sir John Brown & Co., Sheffield.'

In further justification of my presumption, I may explain that, when I wrote this letter, the subject had been recently discussed at the Chemical Society, and a report by Dr. Miller, Dr. Mallet, and Mr. Kirkaldy had been published. (A reprint of this appeared in the 'Chemical News' of February 19, 1869.) Professor Miller, M.D., F.R.S., Assayer to the Royal Mint, was then one of our highest chemical authorities, and knowing, as I did, that some of his conclusions, backed by Dr. Mallet, Dr. Paul, Mr. Kirkaldy, and others, would lead to very serious consequences if practically acted upon, I should have been guilty of culpable negligence or cowardice had I failed to

protest against them, although my scientific position was then a very humble one compared to that of the men I presumed to instruct.

The dangerous conclusions are indicated by the passages in the following extracts from Dr. Miller's report which I have indicated by italics. To what extent the dreadful catastrophe of the Tay Bridge may have been due to this reliance upon tensile resistance to mere pulling strain, without regard to vibratory shock, I will not venture to estimate, but have no doubt that such reliance is specially calculated to evolve such consequences.

Dr. Miller said: 'The wrought iron made in my presence from Cleveland and Northampton pigs, and tested for tensile resistance also before me, bore a rupturing strain of 23 tons per square inch, and an elongation of nearly one-quarter of the original unit of length. *It is, therefore, iron of great strength and toughness. It possesses those qualities that best fit iron for artillery, armour-plates, and iron ships or boilers.*'

Readers should note the '*therefore*' in the above, indicating full reliance in the slowly-applied rupturing and elongation test.

The next paragraph of the Report is as follows:—

'The tilted cast steel, also made in my presence from the very same pig-irons as the above, bore a tensile strain at rupture of above 42 tons per square inch, with an elongation of one-twelfth of the unit of length. *It is, therefore, a remarkably tough and fine quality of steel, well suited for rails, ship-building, and other structural uses.*'

'*Therefore*' again. According to what I *then* dared to assert in contradiction to these high authorities, such great resistance to such tensile strain proved *unfitness* for either rails, ship-building, or other structural uses. It is

satisfactory to know that such steel, if *now* offered to the Admiralty for these purposes, would be summarily rejected, for the reasons I then so heretically urged—viz., that, beyond a certain limit, further increase of tenacity is a measure of weakness, an indication of liability to fracture, due to glass-like brittleness.

At the Atlas Works I regularly acted upon this principle. A sample ingot from every Bessemer blow was sent to the laboratory (sometimes as many as thirty per day); its carbon was there determined, and these determinations were checked by mechanical tests. When the carbon—and consequent resistance to tensile strain—exceeded certain limits, all the steel in that blow was condemned as unfit for rails or *structural purposes*.

On one occasion my report was neglected, and a condemned sample sent to Woolwich, and used for rocket-cases, a purpose demanding specially soft steel—steel that would give way at about half the 42 tons of Dr. Miller's sample. One of these rocket-cases burst, and the men around narrowly escaped. Fragments were sent to Sheffield, and a re-analysis (made November 2, 1868) enabled me to recognise and trace the steel to the condemned blow.

I now (1890) add to the above, that I never doubted the accuracy of the analyses of Dr. Paul and Dr. Miller. On the contrary, both were chemists on whose ability, as chemists, I placed especial reliance; and I may add for what it is worth, that their analyses were confirmed by my own, as I witnessed several trials of the Heaton process at Langley Mill, and carried samples of the results to Sheffield, where I tested them both chemically and mechanically.

At first, when I had only tested them as Dr. Paul and

Dr. Miller did, I was disposed to come to the same conclusions as theirs—probably should have done so had I stopped there; but instead of this, I appealed to the practical workman, and had some tools made from this highly-tenacious and moderately-extensible phosphorised steel. The result was very instructive.

Of the six samples obtained, two were thus practically tested: one which contained the largest proportion of phosphorus, viz., 0·24 per cent., and that which contained the least, viz., only 0·05 per cent. The first was made from the inferior pig produced in the neighbourhood of Langley Mill; the second, from pig of good quality, containing but little phosphorus.

The first contained 1·1 per cent. of combined carbon, and was much harder than ordinary cemented steel with the same carbon percentage. It could not be forged into any sort of thin cutting-instrument or tool, such as a penknife blade or small drill; nor could it be hammered into a thin plate without cracking at the edges. It resembled the early samples of Bessemer steel that were made before the important step of using hematite iron was taken, and for the same reason. The second sample was an altogether softer steel, and worked fairly well.

I hope the reader will not be impatient if he meets with some reiteration of my urgency in directing attention to vibratory shocks in structural steel.

Until the publication of my letter in the 'Chemical News' it was generally overlooked—its importance not at all understood by practical engineers. Even now, in this 'age of steel,' it is most dangerously neglected.

APPENDIX

THE following is the Report of the Proceedings of the Chemical Society, January 21, 1869, which appeared in the 'Chemical News' of January 29, 1869, and to which frequent reference is made in this chapter. I reprint it fully.

'*On the Connection between the Mechanical Qualities of Malleable Iron and Steel and the Amount of Phosphorus they Contain.* By Dr. B. H. PAUL.

'It is generally considered that very small quantities of phosphorus in malleable iron and steel are most prejudicial to the quality of the metal. Quite recently an eminent metallurgist has stated as a fact, that much less than 0·3 per cent. of phosphorus produces a decided and injurious effect on steel. The author has, however, been unable to discover any evidence sufficient to justify such a conclusion, and, still less, any reasonable explanation of it. He has recently had an opportunity of testing the truth of this conclusion by determining the phosphorus in some samples of iron and steel made, by the new nitrate-of-soda process, from British pig-iron known to contain phosphorus. Seven bars of iron and two bars of steel made by the Heaton process were examined; their tensile strength and extension had been determined by Mr. Kirkaldy. The iron bars had a tensile strength of from 46,547 to 52,842 lbs. per square inch of area, and an extension, when subjected to this strain, of from 21 to 28·6 per cent. of their length. The two cast-steel bars had tensile strength of 80,916 and 106,602 lbs., and extended to 3·3 and 13·7 per cent. of their length. In the iron bars the author found 0·144 to 0·38 per cent. of phosphorus (average, 0·237 per cent.), and in the two steel bars, 0·24 and 0·241 per cent. The author, therefore, thinks himself justified in asserting that the commonly-received opinion on this subject does not always represent the truth.

'Professor MILLER said he had had opportunities of exa-

mining some of these steels; in fact, he might say that Dr. Paul's experiments had been suggested by himself. He had found, in some careful analyses of his own, very unusual quantities of phosphorus, even in samples of high-class iron—iron which worked well cold, and also at a red and bright yellow heat. It could hardly be doubted that, in many statements of the composition of iron, the amount of phosphorus found had been too low. The old method of estimating the phosphoric acid, which involved the throwing of it down as iron-salt, was unreliable. The phospho-molybdate process employed by Eggertz was, undoubtedly, the best; but even this required the greatest care to avoid getting too low a proportion of phosphoric acid. It was very difficult to ensure the entire precipitation of the phospho-molybdate. One thing was clear from these experiments—namely, that the presence of from two to three parts of phosphorus in 1,000 of iron was not so detrimental as was generally supposed.

'The PRESIDENT (Dr. Warren De la Rue) inquired how the phosphorus existed in the iron, and the form in which it was eliminated during Heaton's process.

'Professor MILLER could not speak with certainty of the condition of phosphorus in the iron; it probably existed as phosphide. It was, however, most certainly eliminated in the form of phosphate.

'DR. PRICE remarked that there was nothing new in the statement that such quantities of phosphorus might exist in wrought iron, but that, with regard to steel, he had yet to learn that 0·24 per cent. of phosphorus could be present without injuring the metal. With regard to methods, he believed that the one at present in use was absolutely correct—that, namely, in which the phosphorus is separated as phosphate of iron, and then determined with magnesia. The molybdate method was excessively tedious.

'MR. FORBES said that in Sweden they would not receive, for making steel, iron which contained 0·1 per cent. of phosphorus. Many works had had to stop for want of ores that

were free from phosphorus. For one mine of such ore there were ten which yielded ore containing phosphorus, and they would most gladly use it if they could. He could not agree with Dr. Miller that the amount of phosphorus in iron was under-estimated. The molybdate process was thoroughly understood in Sweden, and had been in use since 1856. Errors in the estimation of phosphorus could not be due to ignorance of that method.

'Professor MILLER explained that he only meant to say that the molybdate process required care. No doubt the results obtained by Eggertz were perfectly correct. In answer to the President, Professor Miller then gave a short account of the Heaton process. A quantity of the nitre was placed in a wrought-iron pot lined with fire-clay; on this was put a perforated plate of iron, and 12 cwt. of melted cast iron from a cupola furnace were then introduced, with sand and lime; during the reaction fumes, first white, then brown, next grey, were evolved. A violent flame and a roaring noise attended upon it. When again tranquil, the metal was emptied on the floor of the furnace; the slag run out of the pasty mass was pressed between rollers. He was unable to tell the proportion of phosphorus in the slag. The crude cast iron employed contained 1·43 per cent., and the cast steel obtained, under 0·3 per cent. A part, at least, of the phosphorus lost was certainly to be found in the slag.

'DR. PAUL quite agreed with Mr. Forbes that Swedish steel was free from phosphorus. As far as he could learn, there was no other evidence in proof of the injurious action of phosphorus on steel.'

This discussion displays the amount of disagreement, not to say confusion, then existing among eminent chemists in reference to the effect of phosphorus on iron and steel. Other and still more strange examples are quoted and discussed in Chapter IX. To these I may add the following from 'Iron,' vol. vii., p. 655 (May 20, 1876), as a later example:—

'Euverte publishes the results of a series of experiments he has been making on the properties of phosphorus-steel. He finds that rails of this material are of good quality, but need for the development of their maximum resistance an energetic working-up. If they receive this, they are of superior tension to steel rails free from phosphorus.'

The differences of opinion concerning the merits of the molybdate process of analysis may appear still more remarkable seeing that this is a pure laboratory question, concerning which all who discussed it were high authorities, specially qualified to settle at once such a matter of mere analytical fact.

The following communication, made to 'Iron' at about this date, explains the origin of the trouble. I wrote it after passing through a rather humiliating series of failures, which finally proved very instructive, as so often happens when failures are stubbornly studied. In this case they led to the discovery of the relation between the temperature of precipitation and the proportion of nitric acid in the reagent, upon the due regulation of which success or failure mainly depends.

No competent analyst, who will keep this principle in view, and carefully attend to the directions I have given, can fail to obtain satisfactory results by this process, and to do so without any of the uncertainty described by Dr. Miller, or the tediousness of which Dr. Price complained. A long exposure to the steady heat is certainly necessary, but, with the aid of the simple apparatus described and figured, this becomes of little moment, as the slow precipitation then proceeds automatically; it may even be left to itself all night, as stated.

'*On the Estimation of Phosphorus in Cast and Wrought Iron, Steel, and Iron Ore.*

'I was glad to see Mr. Parry's letter on this subject in last week's "Iron," as some able chemists have condemned the molybdate of ammonia method; and I have long been convinced that their objections are but hasty conclusions, based upon insufficient experience. As the determination of phosphorus is of such practical importance, and this method is so simple (and, as I believe, with Mr. Parry, so reliable when proper precautions are used), it is very desirable that those who have given special attention to it should communicate their experience. As my own may possibly be instructive, I state it, as follows:—

'I first used the molybdate according to the method described by Fresenius as Sonnenschein's, the reagent being prepared by dissolving one part of molybdic acid in eight parts of ammonia, to which twenty parts of nitric acid were afterwards added. I used this, as directed by Fresenius, with considerable perseverance and much vexation, the results being so contradictory and unsatisfactory that I never ventured to make any use of them, and was about to condemn the molybdate process altogether when I met with the formula of Eggertz. My great respect for the accuracy and reliability of Professor Eggertz induced me at once to throw my own halting conclusions overboard, and begin afresh upon the molybdate process, following most faithfully every detail of his instructions. The results were quite satisfactory, and by following up the subject I afterwards learned the cause of the previous unsatisfactory and contradictory results. The following is the method of preparing the reagent:—

'The molybdic acid should be first heated with nitric

acid over a water-bath for a few days, in order to convert the B-phosphoric (pyrophosphoric acid), which it commonly contains, into C-phosphoric acid. It must be evaporated to dryness to drive off the free nitric acid. To one part of this molybdic acid add four parts by weight of ammonia of 0·95 specific gravity, and digest in a closed bottle at 16 degs. C. When the solution is thus completed, suddenly add fifteen parts of nitric acid of specific gravity 1·20, still at the temperature of 16 degs. C. This solution must now be set aside, when the presence of any C-phosphoric acid in the original molybdic acid will be shown by the formation of a yellowish precipitate. In order to secure the complete removal of this, I find it desirable to heat the reagent for two or three hours at 40 degs. C. After this the clear solution may be either decanted or filtered, and it is then ready for use. The strictest attention to the above-stated quantities, specific gravities, and temperatures, is necessary, for reasons which I will presently show.

'Having thus prepared the reagent, its application is simple enough, but care is still required:—1. One gramme of the iron or steel is dissolved in 12 cubic centimètres (0·43 fluid ounces) of nitric acid of 1·20 specific gravity. This is best effected over a water-bath. 2. The solution is evaporated to dryness over a water-bath, and then 2 cubic centimètres of nitric acid of 1·20 specific gravity, and an equal quantity of hydrochloric acid, are added, and left for about an hour, until the red, gummy mass is redissolved. 3. Four cubic centimètres of water are now added, and the solution is filtered, care being taken that the filtrate and wash-water do not exceed 20 cubic centimètres. Half that quantity is sufficient. 4. Two cubic centimètres of the reagent are now added for every 0·001 gramme of phosphorus supposed to be present. It must

now be digested, for at least three hours (I have sometimes found six or eight hours desirable), at about 40 degs. C., and occasionally stirred. If no precipitate occurs in the course of one hour, add more of the reagent. 5. The yellow precipitate is now collected on a weighed filter, washed with water containing 1 per cent. of nitric acid, dried in a water-bath, and weighed. It contains 1·63 per cent. of phosphorus. 6. In order to be sure that all the phosphorus is precipitated, the filtrate should be again digested with more of the reagent.

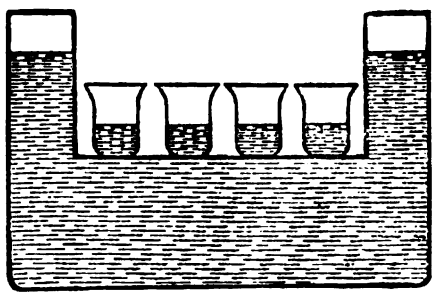
'In applying the reagent, special attention must be given to temperature.

'As already stated, I discovered the cause of my first contradictory results when following Fresenius. I found that a primary condition of success was *an accurate adjustment of the temperature of precipitation to the quantity of free acid present*, and that this depended upon the tendency of molybdate of ammonia to decompose when heated, which tendency is controlled by the presence of free nitric acid (and probably, also, by hydrochloric acid). *A solution of molybdate of ammonia, which decomposes at a certain temperature, will resist that degree of heat, and require a higher temperature for its decomposition, when more nitric acid is added.* At the same time, it is desirable, in order to secure the easy and complete precipitation of the phosphorus, to work at a temperature not far below that at which the molybdate is decomposable.

'The reagent, prepared as above, will bear a temperature of 40 degs. C. without decomposition, but must not be raised much higher. If, however, more nitric acid be added, the temperature may be proportionately raised without decomposition; but then the precipitation is more tedious.

'This decomposition is a serious matter, inasmuch as the molybdic acid is thrown down with the yellow phosphorus compound, and is not distinguishable from it, and thus produces utterly false results.

'The directions in Fresenius are vague and indefinite as regards strength of acid and alkali, and also in reference to temperature of precipitation; and until I had learned the above by my own experiments (suggested by a hint from Eggertz), I had failed to balance the acidity and the



Section of Water Oven.

temperature with sufficient accuracy and constancy, and hence obtained, on one side, an obstinate sluggishness of precipitation, or, on the other, an over-facility and rapidity, accompanied with an excess due to precipitated molybdic acid.

'I suspect that this has been the case with other chemists who have condemned molybdate of ammonia as a reagent for the determination of phosphorus in iron and steel.

'Finding the temperature so important, I devised a very simple modification of the water-bath, for the special purpose of keeping several small beakers at 40 degs. C. for a

long time, and with the smallest possible amount of attention. It was a circular, tin-plate vessel—a saucepan with double sides and false bottom, as shown in section in the figure. The space between the two bottoms and the two sides being filled with water, and the whole heated by a gas-flame, the dry, open cavity within forms a sort of hot-air bath, the temperature of which is easily regulated, so that the contents of the beakers therein may be maintained at 40 degs. C. Having once determined the heat of the water required for this, a thermometer is only needed in the water-jacket, a hole being, of course, left for this and for filling. As every degree of variation in the water produces only about half as much variation in the beakers, it is easily regulated, and the beakers are kept dry outside, and thus easily handled. I have frequently left this little water-oven all night, after adjusting the gas-flame, without finding more than 2 degs. of variation in the beakers on the next morning. It may be used with or without a cover, and is very useful for drying precipitates, &c., especially for these phosphorus precipitates, which should always be kept well below the boiling-point of water.

'I should add, that one of the great advantages of the molybdate method is the small percentage of phosphorus contained in the precipitate. Being less than one-sixtieth part of the total weight, very small quantities of phosphorus become weighable. W. M. W.'

CHAPTER XIII

TESTING IRON AND STEEL

As shown in the preceding Chapters, mere hardness is no evidence of value in the quality of steel; neither can we rely on its tenacity, as tested by power of resisting a gradually and steadily applied tensile strain. In reference to this popular method of testing, I should add that, other conditions being equal, the tenacity thus indicated varies, up to a certain point, with the proportion of carbon contained in the steel; or, generally speaking, with its hardness, even though this hardness be produced by such mischievous impurities as phosphorus, sulphur, zinc, arsenic, silicon, &c. How, then, are we to test the quality of steel?

The reply to this question, of course, demands a previous question—viz., what sort of steel is to be tested, or for what purpose is the steel to be used? Now that we have so largely extended the range of our uses and definition of steel, the previous question becomes the more significant.

I will, therefore, in the first place, limit the inquiry to *tool-steel*, which still remains the most costly, and demands the greatest skill and the best material for its manufacture. It is the truest and the best steel, if we include with it, as usual, the steel used for watch-springs and similar delicate purposes.

It is only fair to state, at the outset, that in treating

this subject I am about to use very freely the information contained in a little, unpretending, but very valuable book, published more than twenty-five years ago, on 'The Management of Steel,' by George Ede. I know nothing more of the author than is to be learned by reading his book. Testing its statements by my own experience I find that Mr. Ede is not a mere college-taught scientist, like too many of those now offering themselves as professors of 'technical education,' but that he writes with full practical knowledge of his subject—a kind of knowledge far more difficult to obtain than the book-lore demanded as the qualification for scholastic university degrees.

Something may be learned by examining the fracture of steel—the 'grain,' as it is called—and many profess to know all about it by such examination, especially when aided by a magnifying lens. I have tested the decision of some of these 'knowing ones,' and have detected very curious blunders. These, however, were cases where the knowing one professed to see differences or peculiarities quite invisible to ordinary eyes, either with or without the magnifier.

Some of the fracture-indications of bad steel are easily understood, such as coarse grain approximating more or less to that of cast iron, and exhibiting what in the North are called 'twuds' eyes,' or 'toads' eyes'—little hemispherical or cup-shaped cavities, in which have evidently resided bubbles of some kind of gas. Where these are visible, the steel is either intrinsically bad or has been 'burnt.' The nature of such burning is explained in the next chapter. In all cases the grain should be close and fine, presenting a dull, silvery appearance, with a tendency to fibre at the bending side of the fracture, if annealed. The general texture is closer when hard than when annealed. In

either case it should have a uniformly white colour, with entire absence of sparkling particles. Although good steel always presents these features, it is by no means certain that all samples with a fine, close grain are good. Therefore, further testing is necessary.

Supposing the fracture to be promising, this further testing may be effected by forging it to a fine point, after having determined what degree of heat the sample will bear without incipient fusion or damage by burning. This will vary according to the composition of the steel: the harder it is, or the more carbon it contains, the lower its fusing-point, and the less heat it can bear without incipient fusion and the partial combustion of its carbon. The consequences of these actions are its falling to pieces or crumbling under the hammer, which will happen to the very best cast steel when overheated, such high-quality steel being more liable to this overheating than inferior shear-steel, simply because it contains more carbon. It will thus crumble even at a bright-red heat, while low carbon shear-steel (otherwise called 'blistered' steel) may be raised without damage to nearly a white heat.

This question of heat being answered, the hammering or 'drawing out' should be conducted at a temperature distinctly below that at which mischief commences. If, for example, the steel will just bear a bright-red heat, the forging test should be applied at a cherry-red heat. If the steel is of fine quality, it will bear beating or 'drawing under the hammer' to a point as fine as a needle; if inferior, it will not take so fine a point, but will split. Steel that cannot be thus forged to a point cannot be ground to a fine edge, however it may be hardened and tempered.

As Ede says, 'drawing a piece of steel to a point for

testing is a very simple process; but, simple as it is, without some degree of attention it may produce false results, and mislead the unwary. For instance, suppose we were to take a piece of steel cut from a bar, and commence to draw the extreme end of it to a point; if the extreme end of this piece of steel should happen to be, even in a small degree, concave previous to hammering it, we cannot succeed in getting a fine, sound point, although the steel should be the best that Sheffield can furnish; for, in hammering it, the surface steel will overrun the centre, and cause the extreme end to be concave in a greater degree, and as long as this concavity exists in the end the steel cannot take a fine, sound point.'

In case this should not be understood, I may add that Mr. Ede means by 'the extreme end' the face of the fracture. When a piece of steel is broken, it frequently happens, especially to steel of the highest quality and finest grain, that the fracture is, to some extent, what mineralogists call 'conchoidal,' or shell-like—*i.e.*, one face is convex, the other concave.

It is evident that, if the concave end is operated upon, the greater extension of the surface due to hammering will increase the superficial overhang, or deepen the terminal concavity, and thus produce, at last, a tubular point instead of a solid one. To secure the necessary solidity of the point, Mr. Ede recommends that, 'previous to commencing to draw the steel to a point, the extreme end of the piece of steel under trial may be either ground or filed to a rounded point similar to a centre-punch, but not quite so sharp.' It is evident that, starting thus, the point thrust forward by the forging will remain solid, and thus the trial will be a fair one. It need scarcely be added, that to apply this test some amount of mechanical

skill and mechanical judgment are necessary, besides experience of what good, bad, and indifferent steel will bear.

This trial does not touch the question of the hardness of the steel, which, supposing it to be composed of iron and carbon only, depends on the proportion of carbon it contains. As few have the skill and appliances for chemically estimating such percentage of carbon, I will borrow still further from Ede, as he supplies rough-and-ready, but really practical, methods of determining such hardness with ordinary workshop appliances.

Referring again to the above-described trial, he says: 'The fine point of this piece of steel under trial may now be cut off, and the steel drawn out again, under a low heat, to a gradually-tapered, square point, but not so fine as before. It must then be plunged suddenly, at this heat, into pure, cold water. The hardened point may then be tried with a smooth file; but I may state that this mode of trial with a file is defective, as files differ in hardness, and only serve to tell us in an imperfect manner the hardness of steel. But if the point be broken off just enough to show the fracture, and it will easily scratch glass, it is a positive proof that the steel is hard, and possessed of good hardening properties. The power used in breaking affords some knowledge of the tenacity of the steel. The broken point may be tried, and the degree of the tenacity of the steel ascertained, by placing it upon a piece of hard cast iron, and crushing it under the face of a small, hardened hammer. If the steel is good, it will resist the crushing, and will cut the hammer's face, and bury itself in the cast iron.' Inferior steel thus tested will, if hard, be crushed to powder; if soft, crushed out flat, and will not enter the cast iron in either case.

To this test of Mr. Ede's I must add a necessary criticism. When he uses 'a piece of hard cast iron' and the face of a 'hardened hammer,' he encounters the same difficulty or uncertainty as that which he describes as pertaining to the ordinary method of testing hardness by trying with a file. The variations in the hardness of hard cast iron and the hardened faces of hammers are considerable—even greater than those of ordinary files. Files of good make vary but slightly, and if the file has been in use, the workman will know whether it is unusually soft or hard. Glass also varies in hardness.

To apply this crushing test satisfactorily, it is necessary to set aside a special anvil and hammer for the purpose. With such a standard at hand, and experience of the behaviour of known samples when tested by it, the quality of others may be determined roughly. I prefer to use one of those small, steel mortars that are sold under the name of 'crushing-mortars,' or 'diamond-mortars.' The mortar is a cylindrical block of steel, with a cylindrical bore, flat at the bottom. Into this bore the steel pestle is accurately fitted, and rests evenly on the bottom of the bore. It is provided with a round head, upon which the blow of a hammer is to be delivered when it is used.

The behaviour of a fragment of steel when placed in such a mortar, and the pestle is struck with a hammer, is very instructive. Bad steel, moderately hardened, will crush to powder; good steel, moderately hardened, will resist, with a slight indication of flattening. Very good steel, highly hardened, will resist, and mark the pestle and mortar with more or less of an indentation, according to the quality of the steel of which they are made. This indentation test is really a trial of the relative hardness of the material of the pestle and mortar and that of the

sample which is tested, and therefore is but relative, and as much dependent on the quality of one as of the other. It is only by practical acquaintance with the character of the particular tool used, especially of the pestle, that this test can be relied on. He who uses it must also be skilful in hardening the steel that is to be tested, as the same sample of steel will behave very differently under this test, according to the temperature to which it was raised in hardening.

It must always be remembered, that a given sample of steel increases in brittleness as it increases in hardness: that, hardened at a low heat, it may stand this test, so far as not crushing is concerned, but will flatten more or less. Hardened at a higher temperature, it may crush if of poor quality, or still resist if of high quality; and if very good indeed—better than the pestle and mortar—it will, when hardened to its utmost, resist both crushing and flattening, and will leave its mark on the face of the pestle as a greater or smaller indentation, according to the force of the blow. The face of the pestle after such indentation should be ground smooth again.

I must add, in reference to these tests generally, and to others of similar kind, that no written or oral description can fully elucidate them; they demand practical skill and workshop experience in their application, which mere reading cannot supply, any more than the reading of text-books on chemical analysis can enable anybody to perform a chemical analysis of a sample of steel without practical laboratory training.

Many attempts have been made to test the quality of steel by applying acid to its surface. If slightly-diluted nitric acid be dropped on a piece of steel and on a piece of wrought iron (both surfaces being clean and bright

before the application), a dark spot will be left on the steel, and a bright one on the iron. The black spot is due to the carbon of the steel remaining undissolved on its surface, and simply indicates that carbon is there, but tells us absolutely nothing concerning the working quality of the steel, as may be proved by a third comparative trial, substituting for the steel a surface of common cast iron. This will give the dark spot sometimes described as a test for good steel, simply because such iron contains carbon, and usually has more of it than the hardest steel.

By immersing a sample of steel in weak acid, such as dilute hydrochloric, sulphuric, or nitric acid, and allowing the slow, solvent action to continue, we obtain an 'etching,' as it has been termed, and upon which some have recommended considerable reliance. I have made many such etching experiments, and, although the results were interesting, they proved to be of little practical value. They indicated irregularities in the composition of the steel, to which I shall have to refer more fully when on the subject of the differences between cast steel and shear steel; but a piece of steel that is uniformly bad may thus show out as equal to another which is uniformly good.

The above, as already stated, refers to tool steel; but now that steel is used for so many other purposes, other tests, as varied as the purposes themselves, have been devised, most of them being supplementary to the extension and tenacity tests, and many of them devised by men who really understand the business.

With such adjuncts, the tenacity and tension tests are valuable; without them, they have little value outside of reports for advertising inventions, and the floating of joint-stock companies.

Prominent among the useful tests is the drop-test, as

applied to steel rails. A rail is taken at random from those to be tested, and rested on two supports, at a stated distance apart, with the length between quite unsupported. A weight is dropped from a given height, and the result observed; *i.e.*, whether fracture occurs, or, if bent, the nature and extent of the bending.

It is obvious that this test nearly corresponds to the actual strain that will be put on the rails when struck by the impact of a heavy train, advancing rapidly.

I should add, that prior to this—*i.e.*, in the course of manufacture—the hardness of steel rails is tested by the determination of the carbon in each blow of Bessemer steel, or pouring of other steel, and this is confirmed by a bending test. The rather common notion that steel rails should be hard is a great mistake—would be very serious if acted upon. When I was engaged in such testing, our standard was 0·40 to 0·50 per cent. of carbon for rails, and a little less for tyres. A sample containing a notable excess above the ½ per cent. was rejected as too hard, as it is well understood that such hard rails are dangerous, and, besides, are costly, inasmuch as they groove the tyres too rapidly.

In the early days of steel tyres some bad accidents occurred owing to over-hardness: some of them broke when subjected to the jarring shock which they encounter in passing over the junctions of the rails, and the fragments were flung out with terrible violence.

It would carry me too far away from my main subject to describe in detail the various tests in practical use, some of which are applied cold, others hot. The bending tests are the most important and varied, and consist in bending over plates or rods of specified thickness, and hammering down the bend until it either breaks or lies right over

against the side. It will be easily understood that, the thicker the plate or rod, the more severe is this test, which virtually consists in stretching the convex side of the bend, compressing the concave side, and subjecting both to the vibratory shocks of the hammer at the same time.

Then there are certain favourite tests, such as the 'ram's-horn test'—cutting a notch in a strip of plate 2 or 3 inches wide, and of given thickness, and turning over each side like rams' horns; the flanging tests, punching tests, dishing tests, welding and bending tests—in which a bend is made upon a weld; and a multitude of others, that are usually specified in giving a large order. In some cases these are more fanciful than useful. I have seen some such included in the specifications of foreign Government contracts; but I must add, that all from our own Admiralty and Ordnance Departments that I have had opportunity of practically examining have been excellent.

In spite of the curious revelations that occasionally burst upon us—usually when the newspapers are ill-supplied with horrible murders and Parliamentary reports—I believe that the British Government, on the whole, is better served in all varieties of iron and steel than any other in the world, and this will appear with terrible effect if any of the latter ever dare to force upon us a great naval war, the issue of which must now so largely depend upon the quality of the iron and steel used by the respective combatants.

As an example of the demands of our Admiralty, I quote the following description, by Mr. Riley, of tests applied before entering upon a contract with the Landore Siemens Steel Company for plates, angles, and beams to be used for the construction of two armed despatch vessels, the 'Iris' and the 'Mercury,' at Pembroke Dockyard.

'HOT FORGE TESTS

'A piece of ½-inch plate, subjected to the ram's-horn test, the lower end being doubled close while cold.

'Shearings of ½-inch plate, about 1½ inch wide, welded together, and bent in the weld to a radius of ¾ inch.

'Two pieces of plate welded together, and bent in the parts welded, one to an angle of 90 degs., and the other to an angle of 105 degs.

'A box-end, made from ½-inch plate to form angle-steel, 3 inches by 3½ inches by ½ inch.

'An outside corner, made from ½-inch plate, welded to angle-steel.

'Two pieces of plate, 2½ inches by ½ inch, welded together straight, then turned after its edge to form a circle 6 inches in the clear.

'Two pieces of plate, 3 inches by ½ inch, welded together, and bent off at right angles.

'A piece of plate, 21 inches by 10 inches by ½ inch, turned to the form of a tube (not welded), then placed in a flanged socket, and a flange-pin forced into it by blows from a 60-cwt. steam-hammer.

'A piece of ½-inch plate, 12 inches in diameter, forced into a socket, by blows from a steam-hammer, to the form required.

'A piece of ½-inch plate, dished, and then flattened back nearly to its original form.

'A piece of ½-inch plate, 12 inches in diameter, forced into a tube, then flanged back on the anvil to the form required.

'An outside and inside corner, made from angle-steel, 6 inches by 3½ inches by $\frac{7}{16}$ inch, welded together.

'An inside corner and box-end, made from angle-steel, 6 inches by $3\frac{1}{2}$ inches by $\frac{7}{16}$ inch, welded together.

'A piece of angle-steel, 6 feet 6 inches long by $3\frac{1}{2}$ inches by $\frac{7}{16}$ inch, the web closed together at one end, and the other opened out, and turned back to the form of a ring.

'COLD TESTS

'A piece of 6 inches by 3 inches by $\frac{7}{16}$-inch angle, with the corner bent over, and flattened close by blows from a 20-cwt. steam-hammer.

'A piece of 3 inches by 3 inches by $\frac{3}{8}$-inch angle, 1 foot long, flattened out by two blows of steam-hammer.

'A piece of 3 inches by 3 inches by $\frac{3}{8}$-inch angle, 1 foot long, closed by two blows of steam-hammer.

'A piece 3 inches by 3 inches by $\frac{3}{8}$-inch angle, 1 foot long, flattened by two blows, after which the wings were turned back over the outside angle.

'A piece of 3 inches by 3 inches by $\frac{3}{8}$-inch angle, 18 inches long. After being flattened out, as in the previous cases, the two ends were turned over in opposite directions; the piece was then doubled up in the middle, and closed by hard blows from a steam-hammer.

'A piece of 3 inches by 3 inches by $\frac{3}{8}$-inch angle, 18 inches long, dealt with as the preceding, except before bending one end over the wings were bent back on the outside angle.

'A piece of $\frac{5}{8}$-inch square bar formed into a knot occupying only $4\frac{1}{4}$ inches by 3 inches space.

'A piece of $\frac{3}{4}$-inch round bar formed into a knot occupying only 3 inches by 2 inches space.

'A piece of $\frac{1}{2}$-inch round bar formed into a knot occupying $2\frac{1}{4}$ by $1\frac{1}{2}$ inches.

'A piece of $\frac{1}{2}$-inch steel plate, 12 inches in diameter,

dished to 3¼ inches deep by five blows from a 60-cwt. steam-hammer.

'A piece of 6 feet by 3 inches by $\frac{7}{16}$ inch angle had the wings closed in; it was then placed edgewise on bearings 5 feet apart, and bent by hydraulic pressure to a deflection of 12¼ inches.

'A piece of plate 3 feet by 3 feet by ½ inch had an iron block placed under each corner, 9 inches from the edge, and an iron ball, weighing 1291 lbs., was dropped on the centre from a height of 30 feet.

'A beam piece, 4 feet 6 inches long, made of $\frac{5}{16}$-inch plate, 5 inches deep, with double angles, 2½ inches by 2½ inches by $\frac{5}{16}$ inch, on upper and lower edges, riveted together with ⅝-inch rivets, 3½ inches diameter apart, bent under hydraulic pressure to the form required.

'A piece of ¾-inch plate, 12 inches diameter, forced by hydraulic pressure through a ring 10 inches in diameter, and dished to the form required—that is, 3½ inches deep—by a pressure of 145½ tons, without fracture.

'A piece of ⅜-inch plate, rested during experiment upon a perfectly horizontal surface of an annular iron anvil, a central, circular portion of the plate, 12 inches in diameter, being unsupported. The anvil was firmly embedded in the ground. A charge of 18 ounces of compressed gun-cotton was suspended over the centre of the plate, an air-space of 3 inches intervening between the upper surface of the plate and the base of the charge. The charge was exploded by detonation. The result was that the plate is dished out to the extent of 1½ inches, but there is no sign of fracture.

'A piece of plate, $\frac{11}{16}$ inch thick, supported on anvil as above. Charge of gun-cotton, 10 ounces, and 3 inches in diameter, placed upon the upper surface of the plate, in a

central position, and exploded by detonation. The result was that a hole 1½ inches in diameter is made in the centre of the plate, and that for ¾ inch all round this hole the plate is beautifully cupped or countersunk, as if it had been done by a cutting-tool. There is no lateral fracture in the plate.

'A piece of plate doubled close up, fourfold, without fracture.

'A narrow strip of plate, 2 inches by ½ inch, twisted into the form required.'

Besides the above, the following is quoted by Mr. Riley from the Admiralty requirements:—

'From every plate made a strip is to be cut, which, after being heated to a "cherry-red" colour, shall be plunged into water having a temperature of 82 degs. After being thus cooled, the strip is to be bent, without fracture, until the radius of the inner curve equals not more than 1½ times the thickness of the strip. This is known as the "tempering test." Further, from each lot of fifty plates or angles a piece is to be taken, and, the edges having been planed parallel, its tensile strength is to be proved. To be satisfactory, this must not exceed 30 tons, or be less than 20 tons on the square inch; and before fracture takes place there must be an elongation of not less than 20 per cent. on 8 inches of its original length. These tests are applied in the presence of a resident representative of the Government.'

I am writing this at the end of 1888, when the country is greatly exasperated by learning that at Suakin some of the swords of our British cavalry broke at the hilt, leaving brave men to be helplessly slaughtered. The following is a cutting from a daily paper:—

'An interesting correspondence on the subject of swords

and sword-bayonets has just been issued by the War Office. We trust it may set at rest the vexed and vexatious questions of foreign importation of "corkscrew" bayonets and swords that snap at the first serious test in actual warfare. The manufacture of swords and bayonets lately became almost a lost art in England. If other nations should also lose the art, we might congratulate ourselves on the approach of the happy time when men shall turn their swords into ploughshares and their spears into pruning-hooks. But while the English were losing the art, the Germans (who would have been much more usefully employed on their music and metaphysics) were bringing it to perfection, and Solingen was snuffing out Brummagem. At last, however, a Solingen is rising in Chelsea, and to the Chelsea firm of sword and bayonet makers the Government have been giving contracts which otherwise might have been sent abroad. It was represented that, after all, the Chelsea makers were importing from abroad; and the complaints on this score are the subject of the correspondence to which we have referred. The Chelsea manufacturers show that they have merely been compelled—owing to the want of skilled labour and special machinery in this country—to import certain portions of their weapons from abroad; and the War Office authorities express themselves fully satisfied with the explanation, as, indeed, they well may. In a little while, it seems, there will be no necessity for these partial importations. With a revival of the manufacture in England, we may hope to hear the last of bayonets bending as if they were made of pewter. Bogus weapons nearly caused a frightful disaster in the Bayuda Desert, to the column marching for the relief of Gordon; and in the fight of last week, English Hussars lost their lives because their swords were badly made.'

I know nothing of the Chelsea firm, but do know that we have sword-makers and bayonet-makers superior to any outside of this island: also, that no amount or kind of 'skilled labour and special machinery' can produce good weapons or good tools from bad steel; by bad steel I mean the Bessemer rubbish and Siemens-Martin rubbish which has of late been used to such a shameful extent in the manufacture of weapons, cutlery, and tools.

I call it 'rubbish' in reference to such uses, though it is good enough for rails and other heavy purposes. It is now almost impossible to obtain a table-knife or other knife, or other article of cutlery, that will compare in quality with those made thirty to fifty years ago; the reason being, that the old-fashioned Sheffield pot-steel, made from the purest of Swedish charcoal-iron, is almost as costly now as it was then. Referring to the price-current for present week (the last of 1888), I find that the best cast steel is quoted at 60*l.* per ton, while 'steel cross-ends' are quoted at 2*l.* 7*s.* 6*d.* or 2*l.* 10*s.* per ton; heavy steel rails, 4*l.* 2*s.* 6*d.* to 4*l.* 10*s.* The cheapest—the ends of rails that are sawed off to bring them to gauge length, and the ends of steel plates that are sheared off for the same purpose—constitute the raw material of the fraudulent substitute for true cast steel. This substitute is cheaply obtained by simply melting the scrap in Siemens' open hearth or other suitable furnace, and hardening it as demanded by the addition of spiegeleisen.

Such material, instead of having the combined hardness and toughness of the old-fashioned pot-steel made from the best brands of pure Swedish charcoal-iron, cemented with pure charcoal, and then melted in crucibles, is, according to the quantity of added spiegeleisen, either the soft material of the twistable bayonets, or the brittle

abomination of the breakable swords. Even worse than this is the result of 'hard blows' which are occasionally obtained directly by some mistake in the course of Bessemer work, and condemned as unfit for rails, tyres, &c. When I was engaged in testing the Bessemer work at Sheffield, all such ingots were set aside for ploughplates, and sold accordingly; but he would be a bold man who should assert that they were used for no lighter purposes.

The whole secret of the celebrated Damascus and Toledo blades, &c., is that they were made of the purest charcoal-iron, containing the exact proportion of the purest carbon that was required to give just, and only just, the necessary amount of hardness; and this material was skilfully tempered.

There still exists abundance of pure magnetic oxide and sufficient charcoal for the production of similar material, and in this country a corresponding abundance of skilled workmen; but such material is costly, and such workmen must be well paid.

As 60*l.* per ton is 60*s.* per cwt. (not quite 6½*d.* per lb.), the difference between the cost price of a sword or bayonet made of rubbish and one made of the finest Sheffield steel is so small, that the economy or fraud prompting the use of anything but the very best material is simply contemptible; but, in spite of this, it is perpetrated under the pressure of modern competitive estimates, and probably will continue to be perpetrated more or less while contracts are made as at present.

The remedy that I venture to suggest is that, if Government must put out such work, it should supply its own material, making the substitution of any other material an act of treason-felony, and sternly applying the punish-

ment to the first offender, the counterfeit sword being regarded by the eye of the law in the same criminal light as a counterfeit sovereign. Measured practically by its injury to individuals and to the State, the crime of counterfeiting steel is far worse than that of counterfeiting coins. The steel itself should be made right through under strict inspection by a competent and responsible Government officer, and finally analysed and tested before being given out.

CHAPTER XIV

BURNT IRON AND BURNT STEEL

THIS subject is intimately connected with the preceding chapters, and is one respecting which some curious notions have prevailed. The following is a Paper which I read before the Chemical Society, April 6, 1871:—

'On page 7 of Dr. Percy's treatise on the "Metallurgy of Iron and Steel" he quotes the following conclusion of Mr. Riley: "The property of becoming useless after exposure to a welding-heat appears from the above experiments to be a special character of fused wrought iron. The experiments have not been carried far enough to lead to any explanation of this; it may, probably, be due to the absence of a small quantity of carbon usually present in wrought iron. In Bessemer's iron" (Mr. Riley believes) "there is no carbon, yet it certainly welds, though not very well."

'Iron which has thus been damaged by re-heating is designated "burnt iron" by the workman, who also gives the same name to iron which has been excessively heated, and exposed *after balling* in the puddling-furnace. It is worthy of remark that no amount of heat applied to the iron in the blast furnace, or in the early stages of the puddling process, produces burnt iron.

'Burnt iron is brittle; its fracture is short, and what is

called crystalline; it has lost the fibrous character and silky appearance of good iron.

'If steel is raised to a bright-red heat, and suddenly cooled, it is rendered hard and brittle; but this hardness may be modified, and brittleness diminished, by the well-known process of tempering. If, however, the steel be raised to a yellow or white heat, and then suddenly cooled, it is no longer capable of being tempered by mere re-heating; it remains permanently brittle, and is worthless for the ordinary uses of steel unless it is again raised to a welding-heat, thoroughly rolled or hammered while hot, and then allowed to cool gradually.

'The fracture of burnt steel presents a very "coarse grain." It displays in a marked degree the so-called "crystalline" appearance. A careful examination, however, reveals something beyond a merely crystalline structure, for the facets of the aggregated granules have a more or less conchoidal or rounded form. This has been observed by practical men, and the name of "toads' eyes" has been given to the concavities.

'As brittleness and granular or "crystalline" fracture, and even toads' eyes, may be due to other causes, it is sometimes of considerable practical importance to be able to determine whether certain defects of a particular sample of iron or steel are due to original defects of the raw material, or to the carelessness of the workman, who may have burned the iron or steel in subsequent stages of working.

'When engaged as chemist to large ironworks, I was very anxious to be able to solve this question, but for a long time was unsuccessful. Karsten's theory, attributing the change to the absence of carbon, was shaken by the case of the burnt steel. This was also the case with the obvious explanation that the burning is due to oxidation.

'An accident finally removed a portion of the theoretical difficulty, and at the same time suggested a practical method of testing for burnt iron.

'An important part of my laboratory duty consisted in determining the percentage of carbon in Bessemer steel. Each blow was thus examined daily. Besides the determining the carbon of the raw ingots, I frequently had to do the same for samples of rails, plates, tyres, and miscellaneous manufactured steel. As many as thirty or forty of such determinations were frequently made in one day. On one occasion a trap was laid to catch the chemist by an excessively "practical" man, who was displeased by the detective revelations of the laboratory. Two samples of borings, marked A and B, were sent for the carbon of the "*steel*" to be determined. My assistant reported that neither contained more than a trace of carbon; that neither sample was steel, but both were iron. I then re-examined them myself, and observed that they behaved very differently on the application of the standard of nitric acid used for solution.

'When the acid was applied to sample A, the liquid *at first* became unusually dark, suggesting a very large proportion of carbon. This colour gradually became less marked, and finally disappeared altogether when the solution was completed. I found no indications of carbon at all. Sample B behaved in the usual manner of good iron, and only indicated a small trace of carbon, too small to be quantitatively determined by the colour-test.

'Suspecting the presence of oxide in sample A, I repeated the experiment more carefully, and then observed that the dark colour of the liquid was due to suspended particles, kept in suspension by the effervescence, and that these particles were finally dissolved.

'Further examination proved that they were particles

of oxide of iron entangled amidst the metallic iron. On inquiry, I learned that the samples were borings taken from the opposite sides of an armour-plate, one side of which was burned, and the other side good. Sample A was from the burnt side.

'I afterwards obtained samples of iron burnt in different degrees, from such as were just perceptibly damaged, to others that were quite rotten; and I found that in all cases there was a small quantity of oxide in the burnt iron, and that I could readily detect it by the very simple method of putting the borings into nitric acid diluted to the specific gravity of 1·20. The burnt iron always gave a dirty appearance to the acid, *which afterwards disappeared.* This appearance is quite different from that presented by the acid in which similar borings of good iron have been placed. With a little practice in observing the normal appearance of good iron, the difference is easily detected, and thus a valuable practical laboratory test for burnt iron is afforded.

'This test is only applicable to borings from samples of clean, finished, wrought iron; the silicon, graphite, and other impurities of pig-iron, produce a similar dirtiness, which might be mistaken for that produced by the oxide. The dark colour produced by combined carbon is so different in its appearance that it is at once distinguishable; besides which, this is permanent.

'I examined samples of burnt steel in the same manner, but no indications of the presence of intermingled oxide were presented. This, of course, was to be expected, as the carbon of the steel must protect it more or less completely from oxidation by heat. It thus appears that, although the mechanical peculiarities of burnt iron and burnt steel so nearly resemble one another, the respective chemical changes effected in the so-called burning are quite different.

'A number of other facts go to show that the burning of burnt iron is simply a process of partial oxidation, and that, therefore, the term burnt iron is philosophically correct. An armour-plate, for example, is made up of a large number of balls or blooms of puddled iron, welded together. It is built up by welding puddled balls into slabs, slabs into moulds, and piling and welding these moulds into plates. These processes include several re-heatings of the iron, and at each re-heating the whole of these great masses of iron must be raised to a full welding-heat.

'The rolling of a 4-inch plate was formerly declared by all practical men to be an impossibility, until a remarkably enterprising man, then scarcely aware of the difficulties to be overcome, undertook to do it, and succeeded, not only in reaching the 4 inches, but ultimately progressing to 14. One of the greatest difficulties to be overcome was the re-heating of these great masses without burning them, and opportunities of earning large wages were offered to the workmen who should superintend these furnace operations successfully. I know an illiterate, black-faced workman,[1] one of the pioneers in this enterprise, who has earned as much as 40*l.* per week by payments received on tonnage of work done under his direction, and have watched with great interest the mode of proceeding of this man, and of others who have successfully conducted such furnace operations. By various devices, the philosophy of which they do not dream of understanding, they subject the iron to the action of a *reducing*-flame only. I have peered into these great reverberatory furnaces or ovens at all stages, scorching my face and inflaming my eyes continually, and, except at quite the early stage of the re-heating, or the preparatory stages of heating the oven-walls, have always found a

[1] Bates, known in Sheffield as 'Fat Bates.'

densely carbonaceous, obviously reducing-flame, to be the only one permitted to play upon the iron.

'One device I may specially mention, on account of its simplicity, universality, and effectiveness. The great doors of the reverberatory chamber, through which the iron is introduced and withdrawn, are made to rise and fall by the action of a counterpoised lever. They are frequently opened to examine the state of the pile, and do not fit closely; there is considerable air-space at the bottom. If this were left open, a supply of oxygen would find its way to the iron within. Without any idea of the philosophy of the practice, the workman places large lumps of coal just inside the doors, in such a position that the entering air must pass them before it can reach the iron. This coal, intensely heated by radiation from the great flame and the white-hot furnace-walls, is prepared to combine with more than all the oxygen that can enter, which thus passes forward as carbonic oxide and aqueous vapour. The puddler uses a similar device. When he has balled-up his charge—*i.e.*, when it is no longer protected from oxidation by its own combined carbon—he closes his damper, and fills up the air-ways of his furnace *with lumps of coal.* He does this most carefully, just at the time when oxidation would be mischievous. He knows nothing about the theory of this admirable device; and, as far as I have learned, no chemist has hitherto explained the philosophy of this carbon-door — why the puddler, instead of using an ordinary furnace-door, so easily applicable, always has an iron ledge or shelf fixed in front of his fire-hole, on which to place the coal for thus blocking it up. The "staff-hole" is also carefully stuffed with coal at the same time.

'Thus it appears that, when iron is unprotected by combined carbon, it is oxidised, not merely on its surface, but

through its whole substance, if exposed at a sufficiently high temperature, and for a sufficient length of time, to the action of atmospheric oxygen. The possibility of such internal oxidation no longer presents a difficulty, the researches of Deville, Troost, and Graham having proved that red-hot iron is permeable by certain gases.

'The Bessemer process illustrates the protecting action of combined carbon in a very striking and interesting manner. Mr. Riley mistakes in supposing that weldable Bessemer iron contains no carbon. I have made repeated analyses of Bessemer metal in which the carbon is reduced to the lowest proportion compatible with coherence, and find that this limit is reached when the carbon is reduced to about 0·2 per cent. in Bessemer metal prepared in the usual manner. The general practical limit is 0·25 per cent. This is well known to all practical manufacturers who are acquainted with the chemical composition of their steel.

'With less than 0·2 per cent. of carbon the Bessemer iron crumbles under the hammer, and if nearly free from carbon it behaves like a piece of coarse sandstone. This is the ordinary condition of the iron at the termination of the "blow," and before the spiegeleisen is introduced. It is then a burnt iron of very exaggerated type, and is quite useless until it has been unburnt by the carbon of the spiegeleisen.

'The introduction of the spiegeleisen displays in a very beautiful manner the presence of the intermingled oxide. When the fused spiegeleisen is poured into the converter containing the fused material, which I shall call the melted burnt iron, a violent ebullition is visible, jets of carbonic oxide are forced through this burnt iron, and a huge, blue, carbonic-oxide flame pours out of the mouth of the

converter. The quantity thus poured forth completely fills the mouth of the converter. It is perfectly obvious that no air is entering at the same time, the blowing has ceased, and thus the only possible source of supply of oxygen for the formation of this great volume of carbonic oxide is within this melted burnt iron. If the quantity of spiegeleisen thus introduced is insufficient to supply a minimum surplus of 0·20 to 0·25 per cent. of carbon, the reduction of the free oxide is not completed, and the resulting product breaks under the hammer from mere want of complete coherence.

'In like manner, when the spongy balls of iron from a puddling-furnace are first crushed down by the hammer, jets of carbonic oxide (to which the workman applies the universal name of "sulphur," issue forth. I have observed that this takes place most abundantly when the ball has stood for some time waiting its turn for the hammer, and believe that it is caused by the commingling of the superficial burnt iron with the inner iron, which remains unburnt, and still retains a small portion of carbon.

'The manufacture of pure iron by the ordinary processes is practically impossible; for, immediately all the carbon is gone, oxidation commences, and iron quite free from carbon will not bear the exposure which is necessary in the processes of forging, still less of fusing. By working in an atmosphere of carbonic acid, pure iron might possibly be obtained.

'The amount of carbon necessary to prevent the iron from becoming burnt varies with the severity of the oxidising exposure. The case of the Bessemer iron above cited is that of the maximum severity of exposure. The idea sometimes expressed, that chemically pure iron would be unfit for commercial purposes, is, I believe, a fallacy.

The nearer it approaches to purity, as regards all but the protective minimum of carbon, the greater its value for all purposes where toughness, malleability, and ductility, are demanded.

'The great art of producing good armour-plates is that of working exactly up to the point where the carbon is reduced to its uttermost minimum, and where another re-heating, even to bright-redness, would produce burnt iron, the iron being also free from other impurities, especially phosphorus.

'I have already shown that burnt steel does not contain the free oxide which, by its presence, destroys the continuity and cohesion of burnt iron. What, then, is the nature of the burning process in this case, and how does it produce the observed mechanical changes? The following facts may assist us to the required explanation.

'When engaged at the works of Sir John Brown & Co., Sheffield, I frequently had to determine the carbon of rails, tyres, plates, &c., made from known samples of Bessemer steel, from ingots of which I had already determined and recorded the percentage of carbon. In every case where I had reliable opportunities of identifying the raw material, I found that the finished rail, &c., contained less carbon than the ingot from which it was made. The amount of difference, however, was variable—was usually the greatest when the steel was the hardest—*i.e.*, when it contained the largest proportion of carbon. This reduction of the quantity of carbon varied from 0·02 to 0·10 per cent. The extreme of these limits was reached in the case of some hard steel plates which, on account of their excessive hardness, were objects of special investigation.

'Now, the steel of these plates, or the ordinary rails, &c.,

is heated only to bright redness, then hammered, heated again, and rolled.

'Another case. Some very brittle plates were made by rolling an unusually hard sample of Bessemer steel containing 0·75 per cent. of carbon. Being engaged in some experiments on annealing, I secured some pieces of this plate, and heated them for periods varying from six hours to four days in an annealing furnace, where the temperature was purposely retained at a dull-red heat. I then examined them mechanically and chemically—determined the carbon of their "skin," and of their interior at different depths from the surface. By the skin I mean the clean metal surface after the scale was removed. This skin was shaved off for analysis by means of a flat-faced drill.

'I found that the skin of the piece of plate which had been heated during four days contained no carbon, or only a trace too small for determination; this absence of carbon continued to a sensible depth—to about the fiftieth of an inch. (Having no means of accurate measurement, this estimate is but an approximation.) Below this a sensible amount of carbon was detected, and this rapidly increased, till at a depth of about one-eighth of an inch it amounted to 0·72 per cent.; and this continued without any sensible variation to the middle of the plate (which was ½ inch thick), and on to within about one-eighth of an inch of the other side.

'All the other plates suffered a loss of carbon from their surface, but in lesser degrees, corresponding to the time to which they had been heated.

'I made several repetitions of such experiments, and found that, by exposing steel to open fires, the removal of the carbon from its surface and interior was much more rapidly effected. I do not bring forward these experiments

as novelties, as I believe that similar experiments have been made by others. My object is to show that the carbon of steel may be oxidised and removed without fusion or *visible* combustion; that a slow combustion of carbon takes place, even at a low red heat; and that this combustion, like the opposite process of cementation, is not limited to the surface, but proceeds gradually inwards.

'The permeability of red-hot steel by oxygen and carbonic oxide enables us to understand the otherwise mysterious action of the interior oxidation of the carbon. Under favourable circumstances, it is probable that a considerable portion of the carbonic oxide thus produced may remain occluded in the iron.

'Let us now suppose that we have a piece of steel at the welding or pasty heat, just at the temperature most favourable for the most rapid endosmosis of oxygen and the exosmosis of carbonic acid, and that, while these actions are in full progress, we suddenly cool the steel, and arrest the possible exclusion of the carbonic oxide. The result must be the production of a certain degree of molecular disintegration and porosity of the steel, the minute, arrested bubbles of carbonic oxide or oxygen producing an effect upon the cohesion of the burnt steel similar to that of the particles of oxide upon the burnt iron.

'The "toads' eyes," or conchoidal facets of the so-called crystals, are in strict accordance with this explanation, as also is the fact that burnt steel may be cured by re-heating and hammering, or rolling at a welding-heat, as at this temperature, and subjected to such pressure, the separated faces of the bubble-holes would be welded together, and the gases either occluded or driven out.

'All steel presents a "grain," or so-called crystalline structure, and this varies in its degree of coarseness: in

highly hardened steel the grain is coarser than in the same quality of steel when tempered or softened.

'My own conviction is, that all steel and all iron is of spongy structure; that such a structure may even be common to all metals; that the so-called crystalline fracture of iron and steel is not due to crystallisation at all, but to a visible degree of porosity; and that the fibrous structure of rolled iron is merely due to a different arrangement—an elongation of these mechanical pores. By pores and porosity I do not mean those imaginary interspaces between imaginary atoms, in the midst of which our modern mathematicians so luxuriously revel, but actual, visible, and demonstrable spaces.'

This Paper was curiously received by some of the then active Fellows of the Society; it was regarded as so heretical that they refused to publish it in the Society's Proceedings, and it was not until the president, Dr. Frankland (who did understand it), vigorously interposed, that an abstract was published. Mr. Crookes published it fully and promptly in the 'Chemical News'; so did Professor Cannizzaro in the 'Gazetta Chimica Italiana.' Twenty years of subsequent scientific progress have curiously reversed its original heretical character.

The following is supplementary:—

Old gardeners believe that an old pruning-knife takes and keeps a better edge than a new one. Barbers have similar faith in old razors, and other users of similar edged tools commonly hold a similar belief. By such old tools they mean those that have been much worn, the original edge ground quite away, until the improved edge is formed by what was an interior part of the steel.

I believe that they are right, having verified their conclusions by first testing the edge of a new pruning-

knife, then grinding it away sufficiently to represent some years of hard wear, and comparatively testing the new edge thus exposed. My conclusion is quite in harmony with the established tradition, and, if what I have expounded in the above paper is sound, there is no difficulty in explaining it.

Let us suppose we have a knife-blade which, like a pruning-knife, is thick at the back, and that we heat this to redness, for hardening, in a fire where there is free access of air. What must happen according to the investigations described on page 256?

It is evident that the superficial oxidation will affect the edge—will soften the steel of which it is composed through its whole thickness where it is very thin; but this softening action will not penetrate to the middle of the thicker part of the blade—that is, the part which becomes the edge as the knife grows older and more and more ground or otherwise sharpened away from its original edge.

If any reader regards this as mere theorising, let him take a piece of bright steel, heat it to redness in a common fire, and then plunge it in water, as in ordinary hardening. He will find that the original steely surface is replaced by one of ordinary iron-scale; and if he maintains the red heat for a few minutes, he will find some of this scale chipped off by the sudden contraction of cooling, and may collect it from the bottom of the vessel containing the water. If a practical workman, he may test the hardness of the edge of a thick-backed knife that has been thus treated with a file, and then try the back with the same file, and compare results.

CHAPTER XV

CEMENTATION

I WILL now proceed to the practical operations of making steel, beginning with the roundabout, indirect, Sheffield method, which, in spite of latest innovations, is still demanded for the production of highest qualities of tool and cutlery steel. What I have already argued concerning the composition demanded for such steel—viz., that it must be as free as possible from everything excepting iron and carbon—at once indicates the first essential, viz., that the iron from which the steel is to be made shall be the purest obtainable. Hence the demand for Swedish iron, which is made from the purest ores, smelted with charcoal, of which the famous 'Loop L' brand is an example. Even this has to be deprived of the carbon it contained in its crude state, not because such carbon was objectionable itself, but because it was associated with silicon, which silicon cannot be completely removed without also removing nearly all the carbon.

The pure ores derived from a geological formation anterior to the existence of the remains of vertebrated animals, are not contaminated with the phosphorus derived from the phosphate of lime of bones, and the charcoal fuel is free from the pyrites which charges pit-coal with sulphur.

The mechanical arrangements of the cementing-furnace need not be here described, beyond reminding the reader that it contains the cementing 'chests,' or converting-pots, which are boxes of fire-brick or fire-clay, 10 to 15 feet long, and 2½ to 3 feet broad, and about the same depth; that they are heated under an arch surmounted by the conical chimney which constitutes so characteristic a feature of the architecture of Sheffield. The heating arrangements are all specially devised to attain the object of heating these chests as uniformly as possible with a minimum supply of oxygen and a maximum supply of smoke.

Some of those flippant people whose mission is to set everybody right excepting themselves, who profess to know everything without studying anything, have been very severe in their criticisms of the poor Sheffield steel-makers, have supplied them with patronising hints concerning the wastefulness of not consuming their own smoke, and have urged the improvement of their furnaces in order to ensure complete combustion of their fuel. If these knowing people had condescended to learn something from those whom they profess to instruct, they would have discovered that the devices they suggest for effecting the complete combustion of the fuel in a converting-furnace would of necessity defeat its object—would cause the combustion of the cementing-materials themselves, and prevent the combination of their carbon with the iron; would rather oxidise, or burn it, than convert it into steel.

This will be easily understood when we remember that each chest is charged with—first, a layer of coarsely-ground charcoal (that from hard wood preferred), about 2 inches thick; then a layer of bars (usually about 3 inches wide

and ¾ inch thick), with ½ to ¾ inch space between the sides of each. Over this layer of bars, and into the interspaces, another layer of charcoal is sifted to a depth of about 1 inch above the bars; then another layer of bars and charcoal repeated in like manner up to within about 6 inches of the top of the chest. Then old cement powder —*i.e.*, previously-used charcoal—and 'wheels waif,' or grinders' waste, is moistened, and plastered over this. These arrangements are made to allow the charcoal to be heated to its combustion-temperature, but not to permit its combustion, which, however, would occur, in spite of these precautions, if sufficient oxygen were admitted into the furnace to produce complete combustion of its fuel.

It seems at first sight that this difficulty might be easily overcome by simply closing the chest with an air-tight cover; but this has been found to be impracticable, owing to the gases that are given off from the charcoal, which must be allowed to quietly and gradually escape, as they do, through the porous covering above described.

But what are these gases? If there is no combustion of the charcoal, there can be no formation of carbonic oxide or of carbonic acid; and the charcoal itself is not volatile.

Long ago I encountered this physical conundrum in another form, and, after some study, finally solved it. When experimenting on King's electric light in 1846 (the original incandescent device, of which the modern lamps are but modifications), our vacuum was obtained by blowing a bulb at the top of an elongated barometer tube, in which bulb was sealed a stick of charcoal (gas-retort carbon), about ½ inch long and $\frac{1}{10}$ inch thick. This produced the light by its incandescence. A wire attached

to it, dipping into the mercury of the tube below, made one of the connections; while another wire, going upwards, and sealed into the top of the bulb, made the other. The mercury, of course, stood about 29 inches in the tube, leaving the bulb vacuous. But immediately the connection was made, and the charcoal became incandescent, the mercury fell about 9 or 10 inches below its normal height, and thus remained. Some gas had been given off, and a smoky film on the bulb, near the charcoal stick, indicated combustion. Further investigation confirmed this indication.

But how could combustion occur in a Torricellian vacuum? Whence came the oxygen?

These questions are answered by the fact that, if newly-burned charcoal be plunged while still red-hot in mercury, and then, when cooled, be allowed to rise into a jar of gas standing over the mercury, a very curious contraction of the volume of the gas takes place; it is absorbed by the charcoal, which condenses large quantities within its pores. De Saussure found that a piece of boxwood charcoal absorbed ninety times its own bulk of ammonia, thirty-five times that of carbonic acid, or bicarburetted hydrogen, nine and a half of carbonic oxide, more than nine times its bulk of oxygen, and varying other quantities of other gases.

Thus, charcoal which has been exposed to the air and various vapours becomes a receptacle of gases, and these are given out more or less completely when it is heated, the oxygen supplying material for the combustion of the charcoal itself. The quantity of gas thus occluded in the charcoal of the cementing-chests must be very considerable, and we must not lose sight of it in considering the rationale of cementation. Inventors who devise methods of steel-

making by placing the iron in closed retorts should also be mindful of it.

Let us now consider what occurs to the bars of iron when thus surrounded by charcoal, and kept at about an orange-red heat—*i.e.*, a little below a yellow heat. The furnace is closed, with the exception of the 'tasting-holes,' through which project the ends of some long trial bars; the full heat is maintained for eight or ten days, the tasting-bars being withdrawn from time to time, and inspected, in order to ascertain the progress of the cementation, which is determined by the blisters on the bars and the appearances presented by their fracture. When the carbon is found to have penetrated sufficiently, the furnace is allowed to cool slowly, about a week being demanded for this.

The result is very remarkable. Each iron bar is found to have combined with a considerable quantity of carbon. Its fibrous structure is obliterated, and exchanged for the well-known granular or 'crystalline' structure of steel; scaly crystals in this case. This change is the most decidedly indicated on its surface, and becomes less and less marked at increasing depths towards the middle.

Chemical analyses of borings taken from near the surface, and at different depths, show that these mechanical variations correctly indicate the varying proportions of carbon that have combined with the iron, the outside containing much more carbon than the interior.

The surface of each bar is more or less blistered, the regularity of the blistering being one of the indications of quality. Some kind of gas has evidently been generated within the metal, and this has happened during the active stage of the process, not during the cooling, as proved by the blistering of the tasting-bars, which blistering is one

of the indications by which the workman judges of the progress of cementation. We must not forget this, as it shows that the blistering is an essential element of the process, and not a mere accident, as in the case of the vexatious blistering of plates and sheets of wrought iron.

We are now face to face with the great mystery of cementation. Here are two solids, iron and carbon, in contact with each other, neither of them volatile at the temperature of the furnace; and yet they combine in such a manner that the solid, non-volatile, and infusible carbon shall not merely unite with the solid iron on its surface, but shall actually pass bodily through it—a solid actually penetrating and permeating another solid.

This is not the course of ordinary chemical combination. If we place solid carbonate of soda in contact with solid tartaric acid, even though both be broken up into fine powders, and packed closely in a bottle, as they are in such preparations as Eno's Fruit Salt, Lamplough's Pyretic Saline, sherbet powders, granular effervescing salts, &c., they remain in contact, without combination, so long as they remain dry—*i.e.*, solid. They only combine and effervesce when they become mutually permeable liquids by being dissolved. It is commonly stated, as a general law, that solids cannot chemically combine with each other; they must be rendered either liquid or gaseous by solution, fusion, or volatilisation, before their union can take place.

Some recent experiments have modified that expression of the law, though not the law itself. It is now found that solids may be made to unite completely by mere pressure, provided the pressure be sufficiently great. Mr. W. Spring has produced true alloys by simply subjecting mixtures of the filings of different metals to great pressure —about 100,000 lbs. to the square inch. Thus, filings of

bismuth, tin, and cadmium were squeezed into perfect union, forming a fusible alloy that melted in hot water at 113 degs. Fahr. (99 degs. below the boiling-point). True brass was formed by thus compressing a mixture of copper and zinc filings. True sulphides were formed by compressing metals and sulphur together at 97,500 lbs. per square inch. Magnesium sulphide, zinc sulphide, bismuth sulphide, lead sulphide, silver sulphide, copper sulphide, tin sulphide, and antimony sulphide, all having the appearance and properties of the natural sulphides, were thus formed. These interesting experiments do not, however, contradict the general law above stated, as it appears that the pressure produces actual fluidity, and the combination is effected by an actual transfusion of the substances. Mr. Spring does not appear to have effected the combination of an infusible substance like carbon.

It would be interesting to make similar experiments with iron and carbon, in order to learn whether steel may be thereby produced.

Returning now to the cementing-furnace, and our problem of the penetration of the carbon, one explanation that suggests itself is, that a combination of iron and carbon takes place at the surface, producing a film of carburet of iron; that this film, somehow, gives up some of its combined carbon to the inner film in contact with it, while it is at the same time combining with more carbon from the outside; then the inner film passes some of the carbon thus acquired from the superficial film to another film interior to itself, and at the same time is being supplied with more from the superficial film. This going on deeper and deeper, may by slow degrees pass the carbon gradually towards the middle, and ultimately convert the very core of the bar, as it actually does become converted.

Some such transmission must occur; but how is it effected? What is the *modus operandi*?

I venture to suggest that it is not a transmission of carbon itself, but a transfusion, or influx, or soaking in of carburet of iron; that the carbon first forms a film of carburet on the surface of the bar, and then this superficial film of carburet unites or alloys with a layer of iron immediately in contact with it, forming thereby a lower carburet; that this, again, acts in like manner on the next deeper film, and so on, the outside film in contact with the charcoal always taking up more and more carbon, which is thus passed on inwards until the very core is reached.

This theory, it must be admitted, demands some modification of our ordinary ideas of the solidity of heated iron. Is iron at a welding-heat really a solid?

A little reflection will show that it is not, but is rather in a viscous or semi-fluid condition, like that of heated sealing-wax or red-hot glass. It is this condition that renders welding possible, welding being nothing more than the sticking together of two pieces of such plastic material as two pieces of semi-fused sealing-wax, which adhere and become one piece; or as the glass-maker unites the stem of a wine-glass to the bowl, or the handle of a jug to its sides; or, more familiarly still, as we unite two pieces of plastic or semi-solid clay.

But this is not all: there is another property that comes to our aid while struggling to solve this mystery. The carburet of iron is much more fusible than the iron itself — so much more, that at or near the welding-temperature of iron a highly carburetted compound is actually liquid, and may, therefore, to some extent, though very slowly, soak into heated iron, as zinc and tin soak

into iron in the processes of—so-called—galvanising, and in the tinning of tin-plate.

As most of my readers are, doubtless, aware, these operations of tinning and zincing are not merely superficial: the tin and zinc soak into the iron, which may thus be penetrated through and through, even though of considerable thickness, if left long enough in the bath of molten metal. The action which I suppose to occur has also a close analogue in the diffusion of saline or other soluble matter through a liquid at rest. If, for example, a lump of rock-salt be placed at the bottom of a vessel filled with water, the salt dissolves, and a stratum of brine lies at the bottom of the water. Gradually, in spite of the greater specific gravity of the brine, the salinity rises, and, if sufficient time be allowed, the salt becomes diffused throughout the whole of the water, in spite of every precaution to avoid any stirring or the production of convection currents. We can form a conception of the nature of this action by supposing that there is some kind of attraction or affinity exerted between the salt and the water, and that this is strong enough to overcome the very slight cohesion of the water, and thus effect a flowing through it; or, according to the molecular conception of the constitution of matter, we can imagine the molecules of the salt pushing aside the freely mobile molecules of the water, and thus elbowing their way in obedience to the attraction of the unsaturated water beyond.

According to this theory of cementation, the outer parts of the bar should always contain more carbon than the inner, which is the case; and hence the necessity for further treatment of this 'blistered steel,' which requires to be, somehow, mixed up together, in order to attain anything like uniform diffusion of carbon, and consequent

uniform hardness. The most effectual means of obtaining such admixture is evidently to cut up the bars, and melt the fragments together. This is effectually done in making 'pot-steel' or 'cast steel,' which owes its superiority to the uniformity thus produced.

Shearing, and making the sheared pieces into faggots, then beating these faggots together at a welding-heat, rolling, re-shearing, and re-faggoting, &c., also effects an admixture in the new bar formed by the welding and blending of many bars of the blistered steel together; but the degree of uniformity is far inferior to that obtainable by the more expensive method of casting.

I offer this theory of cementation simply as an attempt to grapple with a very difficult problem, and one which the reader must accept for what it is worth. An alternative theory is discussed a little farther on.

In reflecting on this subject, we must always keep in view the fact that carbon itself has never been fused by human agency, and is certainly infusible in the cementing-furnace, although it confers upon iron an increased fusibility by combining with it.

We know that, if a roll of solid sulphur be pressed against a glowing bar of iron, combination takes place immediately, and that the sulphuret thus formed runs down as liquid, owing to its lower melting-point; but in this case the sulphur becomes a liquid before the combination takes place.

There is absolutely no approach to any such liquefaction of the carbon in the cementing-furnace, not the smallest degree of adhesion among the granules of the charcoal—they are just as dry and brittle and solid at a white heat as when cold.

Neither is the carbon of itself at all volatile. We do

sometimes read of 'carbon vapour' and 'gaseous carbon'; but where or how the writers obtained it, and how they determined its existence, has not yet been explained. I should be delighted to take lessons from those who have produced it, seeing that the condensation of this gas into the crystalline form—that is, the artificial production of diamonds—would become a very hopeful problem with vapour of carbon in hand.

But although carbon itself is so remarkably infusible and fixed, its compounds with other single elements are remarkably volatile. The oxygen compounds, carbonic oxide and carbonic acid, are gaseous under ordinary conditions of temperature and pressure; the hydro-carbons, such as coal-gas, petroleum, turpentine, and the volatile oils generally, are either gases, or are liquids readily convertible into vapour; and that very remarkable compound of carbon with nitrogen, viz., cyanogen, is gaseous under ordinary conditions. The compound of carbon with sulphur, bisulphide of carbon, is a liquid which combines in an abnormal degree great density with extreme volatility. A long catalogue of such compounds might be named.

These facts suggest another theory—viz., that the combination of the carbon with the iron in the process of cementation may be effected by the agency of a gaseous compound of carbon. A number of facts connected with the details of the conditions which the practical workman has found to be favourable to cementation afford support to this theory. They even indicate that, not merely one particular gaseous compound of carbon is demanded, but that the work may be done by one or another of many, or by several simultaneously.

In the first place, the form of carbon used is that of charcoal, the charcoal of hard wood being preferred,

which, as already stated, contains a large quantity of gas condensed within its pores. The gas thus occluded, and heated while in such close contact with the carbon, is most favourably conditioned for combination with the carbon. This applies not only to the oxygen, but also to the other gases, some of which are condensed in far greater quantities than the oxygen.

I have already referred to this occlusion in connection with the necessity of allowing for the escape of gas from the cementing-chest; but its bearing upon the rationale of cementation is so important, that I will now state the particulars in further detail, and tabulated for convenience of reference. The figures below indicate the number of cubic inches respectively absorbed by one cubic inch of boxwood charcoal:—

Ammonia	90	Bicarburetted hydrogen	35
Hydrochloric acid	85	Carbonic oxide	9·4
Sulphurous acid	65	Oxygen	9·2
Sulphuretted hydrogen	55	Nitrogen	7·5
Protoxide of nitrogen	40	Carburetted hydrogen	5·0
Carbonic acid	35	Hydrogen	1·7

These quantities were determined by exposing the charcoal to atmospheres composed entirely of each of these gases respectively. We have yet to learn the proportions in which they exist within the pores of charcoal that has been exposed to ordinary air in the ordinary manner. As ammonia, carbonic acid, oxygen, nitrogen, and hydrogen are usually present, there is fair reason to suppose that these will be appropriated in proportions having some relation to those stated in the table.

The most significant of these is the ammonia, not only on account of the large quantity the charcoal is capable of absorbing, but also in connection with its chemical relations to the iron, and its possible operation in the conversion of

iron into steel. When ammonia is heated in contact with charcoal, its nitrogen combines with carbon, forming gaseous cyanogen, which, in presence of any aqueous vapour, further combines with hydrogen to form hydrocyanic acid (prussic acid), and the acid thus formed unites with another portion of the ammonia to form hydrocyanate of ammonia. If potash or soda is present, cyanides of potassium or sodium are formed. These facts justify us in asking whether gaseous cyanogen or any of its volatile compounds are active agents in cementation.

Graham has shown that such gases may penetrate iron—are, somehow, condensable within its substance or its pores in a very remarkable manner. Cyanogen is a gaseous compound of carbon that is more readily decomposed than hydro-carbons, and far more readily than the oxides of carbon; and, therefore, we may suppose, *à priori*, or theoretically, that it should be a peculiarly efficient agent in cementation.

But when we attempt a direct experimental inquiry, we encounter the difficulty presented by the enclosure of the iron and the charcoal in the sepulchral chest of the cementing-furnace, where all the operations proceed as hidden mysteries. Fortunately, we have another well-known process of conversion, which is conducted in open daylight, and affords very interesting data. I refer to case-hardening, which is a simple and comparatively rapid conversion of the surface of iron into steel, and subsequent hardening of the film thus converted. This conversion may be effected by simply surrounding the iron with powdered charcoal, and heating it for a short time; but, as every practical workman knows, a far better result is obtained by using bone-dust instead of charcoal, and better still by brushing the surface with a solution of ferrocyanide

of potassium (prussiate of potash), evaporating the water, so as to leave a film of crystals, and then heating.

In the latter case we have a direct use of cyanogen combined with potash and a little iron; and in that of the bone-dust we have the raw materials from which cyanogen is produced by heat. (The commercial manufacture of the cyanides is conducted by heating animal refuse, which, like bone-dust, contains gelatine in contact with iron.) I have frequently converted thin sheet-iron into steel by coating it on both sides with the ferrocyanide, and simply heating it in the flame of a candle, spirit-lamp, or gas-light; I have shown this experiment to a class, by first bending the soft iron, and then showing its brittleness after conversion. Leather shavings, or any of the other kinds of animal refuse used in the manufacture of the cyanide, may be substituted for the bone-dust in case-hardening.

Ferrocyanide of potassium is not only used in case-hardening, but also in steel-making. Its use is one of those profound secrets well known to everybody concerned. A large number of patents have been secured from time to time for the use of cyanides and animal substances that produce cyanogen or compounds of cyanogen when heated. Such substances are more used abroad than in this country, and their use is very suggestive of the action of the cyanogen as a carbon-carrier to the iron. The idea propounded by French chemists, that nitrogen is a constituent of the best steel, appears to have been based on the observed usefulness of organic nitrogenous compounds, and of cyanogen compounds, in cementation.

But are there any other gases besides cyanogen and the vapour of its compounds that may be potent agents in cementation? This question has been directly answered by the practical manufacture of steel without the use of

solid carbon. By simply enclosing bars of iron in a tubular case, and passing coal-gas through the tube when the iron is heated, steel may be produced. Gmelin ('Handbook of Chemistry,' vol. v., page 206, Cavendish Edition), after describing the ordinary method, says:—'Or coal-gas is passed over bars of iron heated to redness in a cast-iron tube coated with clay, whereby carbon is transferred from the gas to the metal. When a sufficient quantity of *charcoal* has entered into combination with the iron, the ignition is continued for some time longer, without passing any more gas over the metal, in order that the carbon may diffuse itself uniformly.' The italics are my own, to indicate that, in spite of this direct use of the gas, the idea of its action *as a gas* is by no means entertained.

Some experiments made by Dr. Percy, and described in his 'Iron and Steel,' have a direct and interesting bearing upon this subject.

In the first experiment, two strips of a commercial, thin sheet-iron of very fine quality, 8 inches long and $\frac{3}{4}$ inch broad, were used, their surfaces having been well cleaned with hydrochloric acid, and dried. These were placed in a porcelain tube, and a current of carbonic oxide was sent through the cold tube in sufficient quantity to expel the air. Then that part of the tube in which the strips lay was heated to bright redness during three hours, and carbonic oxide passed through all the while. The tube was then slowly cooled, and the iron taken out. The increase of weight was from 28·96 to 28·97 grains—only $\frac{1}{100}$ of a grain.

This very small quantity may be accounted for by the oxidation of the artificially-cleaned surfaces, which altogether amounted to 24 square inches. They were 'shaded off from blue to yellow from each end towards the

central part.' Dr. Percy thinks it possible 'that a little air might have got into the porcelain tube during cooling, and after stopping the current of the gas.'

This experiment indicates that carbonic oxide conveys no carbon to iron—a conclusion quite in accordance with technical experience. Everything else we know concerning the tenacity with which carbon clings to its first acquisition of oxygen, affords further confirmation.

In another experiment (No. 2) Dr. Percy used a single strip of the same iron, 8¼ inches long, bent so as to form an imperfect tube, and embedded this in the porcelain tube, in charcoal prepared from fine white sugar. It was heated as in the experiment above described, and carbonic oxide similarly sent through the apparatus. The operation lasted three hours. The weight of the iron at first was 29·485 grains, and at the end of the experiment it had gained 0·295 grains. It became brittle after heating to redness and cooling in mercury. It was steel, with 0·99, or nearly 1 per cent., of carbon.

At first glance this experiment seems to show that solid carbon combines directly with the iron; but this conclusion demands reconsideration, seeing that such carbon is accompanied with the condensed gases as already described.

The existence of such gases was shown in this case by an adjunct to the apparatus provided by Dr. Percy. The gas, on leaving the tube, was made to pass through a weighed solution of caustic potash. This solution gained 1·53 grains, due to the formation of so much carbonic acid, which combined with the potash. Assuming, as we may, that in the hands of so skilful an experimenter the carbonic oxide started free from carbonic acid, and received no supplies of oxygen from outside, it must have got its

oxygen from the gases condensed or occluded upon the charcoal.

Other experiments were made, in which hydrogen was substituted for the carbonic oxide. In the first of these (No. 3), the strip was buried in the charcoal to about two-thirds of its length, and only so much was converted into steel, with a gain of 0·69 per cent. on the whole.

In No. 4, the same charcoal being used, and the strip completely buried, the gain was 0·061 per cent.

In No. 5, two strips were used, one of them completely buried in the same charcoal as used in all the preceding experiments; the second strip not embedded, but kept separate from the first by a plug of charcoal. This second strip was placed on the emerging side of the charcoal, so as to be exposed to the gas after it had passed over or among the charcoal.

The first, or embedded strip, gained 0·769 per cent.; the second, or free strip, 0·368 per cent. 'The surface of the free strip was dead in lustre, and somewhat resembled zinc in colour; the surface of the embedded strip was brighter, and of a deeper grey tint.'

Dr. Percy says:—'This result struck me as remarkable. Admitting the purity of the hydrogen employed, the gas must either have taken up carbon in its passage over the charcoal, or a gaseous compound of carbon must have been evolved from the charcoal, notwithstanding its long-continued exposure to a bright-red heat; for it was the same charcoal as used in the previous experiments: or it is conceivable that some dust of the charcoal might have been carried forward, and come in contact with the strip of iron. There was, however, reason to believe that the last condition did not occur.'

In a subsequent experiment (No. 6), presently to be

described, a similar result was obtained when it was absolutely certain that not a trace of charcoal was carried over mechanically. This proves that the hydrogen *per se* had no share in producing the effect in question.

In No. 6 the same charcoal was used again, and in the same manner, except that the position of the two strips of iron was reversed, the free strip being exposed to the incoming hydrogen. The strips were separated by a plug of asbestos, and a considerable interval was left between them. No charcoal could get access to the free strip, and the experiment was continued for three hours, as before. The embedded strip gained 0·559 per cent., the free strip gained nothing. The embedded strip 'became as brittle as glass after plunging it while red-hot into mercury; whereas the other strip could be bent without breaking after the same treatment.'

No. 7.—The same charcoal was used, but pounded finer; it had become very hard. The experiment was continued for four hours. The strip was completely embedded in the charcoal, and gained 0·925 per cent.; but the end first exposed to the gas did not harden.

In No. 8, Experiment 5 was exactly repeated, but extending to four hours, the tube having been carefully sponged out, and the same carbon used. There were two free strips. They gained 0·362 per cent. The embedded strip gained 0·395 per cent.; and its end, which first came in contact with the gas, did not harden.

Experiment No. 9 was made by using a long tube of Bohemian glass instead of the porcelain tube, and strips of electro-deposited iron were used instead of commercial iron. The free strip, with asbestos plugs at both ends, was separated from the embedded strip by a void space of tube 10 inches long, the same carbon used as before,

and the experiment continued for four hours. The free strip, which was at the emerging end, gained 0·251 per cent.; the embedded strip, 1·280.

Dr. Percy supposes that this large absorption of carbon may be due to the loosely-aggregated state of the electro-deposited metal.

In Experiment 10, two long Bohemian glass tubes were used. They were connected by a neck of thinner tube, and laid parallel to each other. In the middle of one—that in which the gas entered—the embedded strip was laid. In the middle of the second tube was the free strip, separated from the carbon by plugs, the two long, free spaces, and by the bent connecting tube, the gas having to pass through these after leaving the carbon, and before reaching the strip. The free strip gained 0·105 per cent.; the embedded strip, 0·513 per cent. Commercial iron was used.

No. 11 was an exact repetition of No. 9, excepting that the hydrogen was passed first through a solution of nitrate of silver in water, and then through pumice wetted with strong sulphuric acid. Electrotype-iron was used. The free strips gained 0·699 per cent.; the embedded strip, 1·062 per cent. In these experiments in the glass tubes the question of whether any particles of fine carbon dust were carried over was tested. The intervening space of the tube was perfectly free from such dust.

No. 12 was another repetition of No. 9, but with charcoal powder that had been washed in hydrochloric acid and commercial sheet-iron. The free strip gained 0·127 per cent.; the embedded strip, 0·192. Both were sensibly hardened by plunging while red-hot in mercury. This was also the case with all the preceding that had gained weight.

No. 13.—Same as preceding, with only one strip of

commercial iron, and that embedded in wood-charcoal, in small particles freed from dust by sifting, and previously heated in a covered crucible during several hours at a high temperature, in a furnace with anthracite as the fuel. This strip only gained 0·0526 per cent., and did not harden by plunging while red-hot into mercury.

No. 14 was an exact repetition of No. 13 in all respects. The increase was 0·0382 per cent., and the strip did not harden when plunged while red-hot into mercury.

Experiment 15 was made with sugar-charcoal (not previously used), but 'exposed during four or five hours, in a covered crucible, to the highest temperature of an assay-furnace heated with anthracite, and in which wrought iron could be melted without difficulty.' Thin sheet electrotype-iron was embedded in this charcoal, and heated for three and a half hours in a current of hydrogen, as in the other experiments. There was no gain of weight.

In connection with these experiments, it should be remembered that similar strips, thus exposed in a heated tube to a current of coal-gas, or vapour of paraffin, or other hydro-carbon gas or vapour, are readily converted into steel. Thin iron wire may thus be converted into steel in one hour.

Dr. Percy's experiments show very clearly that, before passing through the carbon, hydrogen does not act upon the iron, but that after passing through it takes up something which does, and which converts the iron into steel.

What is this? Is it a compound of the hydrogen with the carbon formed in the course of its passage through? or is it some of the occluded gas or gases that were originally attached to the carbon, but swept out by the hydrogen?

All previous experience, as Dr. Percy says, is opposed

to the first view. No compound is known that has thus been formed.

The difficulty presented by the other view is also stated by Dr. Percy, who says that 'it is extraordinary that a hydro-carbon should continue to be evolved from the same charcoal exposed day after day to a strong red heat.'

This suggests a defect in the record of these experiments. We are not told how long was the interval between the experiments, nor whether or not the charcoal was freely exposed to the air during these intervals. The importance of these questions does not appear to have occurred to Dr. Percy. If several hours elapsed, and no precautions were taken to exclude contact with the atmosphere, the old and frequently-used charcoal might, so far as occluded gases are concerned, be nearly or quite as well supplied with them as fresh charcoal. We know that charcoal which has lost its activity as a disinfectant may be revived by exposing it when dry to the air, and we have every reason to conclude that this revival is due to the absorption or occlusion of fresh doses of condensed gas or gases derived from the atmosphere.

Dr. Percy only looks for a hydro-carbon as the possible cementing gas, but, as I have already argued, there are many reasons for supposing that cyanogen may act quite as efficiently as hydro-carbons. Here, however, we still lack direct investigation by experiments similar to those of Dr. Percy's, but made with cyanogen gas only passing over the iron; and we require further examination of charcoal gases in order to determine the combinations that are effected between the gases which charcoal absorbs.

We know that large quantities of the gases are taken in or held by the charcoal, but how they behave to each other when thus packed in such close quarters is at present

but very imperfectly known. The ammonia, which stands first in quantity, and which is so generally obtainable from the air, is quite capable of considerable chemical disturbance, and the experience obtained in the manufacture of cyanides indicates the possibility of cyanogen being formed when it is heated in contact with the charcoal.

The experiments numbered 13, 14, and 15 are very interesting, as showing the impotency of merely solid charcoal when its occluded gases have been driven out. The record would be more satisfactory if it stated the interval between the heating of the charcoal in the furnace and the placing of it in the tube, and whether it was kept well sealed in the covered crucible during that interval. The mention of the covered crucible suggests that it was so kept, but this is not positively stated.

The higher degree of carburisation of the strips that were embedded in the charcoal is sufficiently explained, in accordance with the gas theory, by the fact that, thus buried, the iron would be in contact with the concentrated and condensed gases, which, when swept out by the hydrogen, and carried over to the free strip, would be diluted thereby.

The condition of the ends of the strips nearest to the entering gases, in Nos. 7 and 8, is very interesting. It suggests the idea that the hydrogen there had swept the occluded gases before it in such a manner that they were carried away before they could operate efficiently on the iron.

It would be interesting to repeat these experiments with very long strips, and determine the carbon on different parts of the strip, as may be so easily done by Eggertz's method. We should, probably, find a progressively increasing percentage of carbon up to a certain distance from the entrance of the gas.

CHAPTER XVI

THE BESSEMER PROCESS

THE history of this important invention presents a curious example of a great practical success achieved by great perseverance in spite of starting with a false theory, a theory generally accepted at the time of Mr. Bessemer's early specifications, and which endured for some time afterwards. It was not formally disputed, and the true nature and origin of its fallacy explained, until the publication of my paper 'On Fallacies concerning Steel.'

This theory is succinctly expressed by Dr. Percy, who says:—'If steel be regarded simply as iron carburised in degrees intermediate between malleable and cast iron, then it is obvious that the latter, during its conversion into the former in the processes of fining and puddling, must pass through the state of steel.' It *was* thus regarded; and, as I have already explained, the puddling process was at the same time described simply as a process of oxidation, like that of fining. Dr. Percy's inference expresses this.

On the basis of these theories, Mr. Bessemer describes the object of his invention as 'the more perfect and complete refinement of the iron, whereby it gradually loses the properties common to pig or crude iron, and acquires the properties of cast steel, or of pure or decarbonised iron, while it still preserves such a state of fluidity as will

admit of its being cast into ingots or other desired forms, or articles, by the process of founding. For which purpose I expose the iron in a more divided or extended form to the intense heat of the furnace or furnaces hereinafter described, and to the oxidising action of a blast of air, by keeping such fluid metal in motion, and continually bringing fresh portions of it in contact with oxygen, and with the intensely-ignited fuel, or with the highly-heated interior surface of the furnace, the metal being thus kept in a fluid state until the desired amount of decarbonisation or refinement is arrived at' (Specification No. 44, January 4, 1856).

In Specification No. 232 (October 17, 1856) is the following:—'The air or steam will force its way to the surface, producing considerable agitation of the melted metal, and thus in turn exposing every part of it to the chemical action of the gaseous products passing through it, the oxygen of the air or decomposed steam absorbing rapidly the carbon of the iron, and carrying it off, as also the sulphur and other volatile matters.'

From these and many other passages that might be quoted from Sir H. Bessemer's long series of specifications, it is evident that it was assumed that the blast would do all, especially when steam was added to the air. In No. 44 the action of the steam is particularly described, thus:—'When the crude iron to be refined contains sulphur, I pass jets of steam through the fluid metal. The steam is thus decomposed, producing both oxygen and hydrogen gas; the latter combines with the sulphur, and carries it off in the form of sulphuretted hydrogen, while the oxygen gas combines with the carbon of the crude iron.' This theory of the action of the steam is repeated in later specifications.

It is rather remarkable that, while too much is claimed for the blast of air with steam or hydrogen in removing 'sulphur and other volatile matters,' including 'phosphorus and phosphoric acid' (No. 1938, August 19, 1856), the primary and most effective action of the simple air-blast —viz., the direct removal of the silicon from the iron—is not mentioned, while the use of soda and potash for this purpose is specified. It is evident that this part of the purifying action of the simple blast was not understood, nor the importance of the silicon combustion as a source of heat equal, and in some cases even exceeding, that derived from the combustion of the carbon, as I shall presently show.

The theory upon which the specifications of 1855 and 1856, and some that are later, were so evidently based, was a sound one in the early days of iron-making, when the ores were nearly pure oxides, and the fuel pure charcoal. Then the crude, or pig iron, was merely a compound of iron and carbon, and all that was required to convert it into steel was the burning out of a portion of its carbon; or, to convert it to malleable iron, to burn out nearly the whole.

But since the clay-ironstones and other impure ores have been used, and coal containing pyrites has been the fuel, the whole problem has changed its character. Cort's invention was rendered necessary by that of Dud Dudley.

When Dudley, in his 'Metallum Martis,' described the various seams of ore of South Staffordshire, and worked them with 'pit-coale,' he introduced a complex product—the modern pig-iron—which demands the special treatment, the washing, &c., already described, in order to bring it to the condition of the iron that had previously been obtained by simply smelting the ore, remelting the

cast iron thus obtained, and blowing it with air in the finery.

In like manner, the Sheffield processes of steel-making by cementation became a modern necessity, in order to obtain a quality of steel equal to that which was formerly made directly from the ore by the simplest of apparatus, and used for the famous sword-blades of Damascus and Toledo. We do not make better steel than was made by the primitive ironmasters, and is still made by them in the East; but we make it from inferior materials, such as they could not use at all, and we make it in vast quantities, and with certainty. They made, and still make, but little bits at a time, and these of uncertain quality as regards their proportion of carbon, and consequent hardness.

After long and expensive struggles, which are strikingly displayed in the Patent Office specifications, Mr. Bessemer practically returned, as nearly as modern demands and supply permitted, to the ancient method, plus the use of spiegeleisen. The samples made before this were failures. I tested some of them that were sent to Birmingham. They were both cold short and red short. When an attempt was made to forge a piece, it cracked at its edges as it spread under the hammer, and finally broke to pieces. These defects, as proved by chemical analysis, were due to the presence of sulphur and phosphorus, all, or very nearly all, the sulphur and phosphorus which existed in the original pig remaining in the steel.

The blowing had simply removed the silicon and the carbon. This was done in the old-fashioned finery, but not so effectually on large quantities. The finery tuyères only projected the oxygen of the air on the surface of the melted metal, with but little agitation; the Bessemer blast

sent it throughout the melted mass with thorough and searching effect, and with an effective heating which was unparalleled by any previous device.

The first step necessary for the rescue of the Bessemer process at the critical period of its struggle was the substitution of ordinary pig iron by hematite pig iron. The significance of this is shown by the following results of my analysis of:—1st column, Cleveland pig iron of better than average quality; 2nd column, the average composition of thirty brands of pig-iron used at the Atlas Works, Sheffield, for best iron; 3rd column, the average composition of thirteen brands of hematite iron made for Bessemer purposes, and used at the Atlas Works during the same period—viz., 1868, 1869, and 1870:—

	I. Cleveland pig		II. Good forge pig		III. Hæmatite pig	
Combined carbon .	0·80	1·80	0·711	2·651	0·469	3·188
Graphitic carbon .	1·00		1·940		2·719	
Silicon . . .	2·23		1·913		2·840	
Phosphorus . .	1·30		0·358		0·081	
Sulphur . .	0·27		0·232		0·139	
Manganese . .	0·71		0·382		0·900	
Iron by difference .	93·69		93·464		92·852	
	100·00		100·000		100·000	

It will here be seen, that the greatest difference is in the phosphorus, the quantity per cent. in hæmatite pig being less than one-fourth of that in selected pigs used for making iron of high quality, and only $\frac{1}{18}$ of that in Cleveland pig. In many samples of Cleveland pig the amount of phosphorus is still greater—twenty times as much as in the Bessemer pig. The proportion of sulphur is about half of that in the Cleveland pig, and less than half of that in the good forge-pigs.

I made many analyses of Bessemer pigs on their delivery at the works, and compared the differences of their composition with the quality of the steel produced. These showed that sulphur was far less detrimental than phosphorus to steel, and more mischievous to iron.

It will be further seen, that the total carbon (shown outside the brackets) is considerably greater in the Bessemer than in either of the other irons. This is exclusive of the spiegeleisen, which contains far more than either. The combined carbon is less, while the graphitic carbon is nearly double that of the good forge-pigs, and two and three quarter times that of the Cleveland pig. The difference between the combined and graphitic carbon is simply due to the fact that all the Bessemer irons are grey pigs, usually No. 1. In the best samples, spangles of 'kish' (exuded graphite) may be collected from the cavities with a pen-knife.

This and the silicon—also very high—constitute the fuel which raises and maintains the heat during the blow, and thus gives to the metal that fluidity so necessary for making good ingots, and which was justly and prominently claimed by Sir H. Bessemer in his early specifications as one of the essential merits of his process.

The selection of the hematite pigs was an absolutely necessary step towards the success of the invention as it originally stood—*i.e.*, quite apart from basic lining; but there were yet two other practical defects in the original theory. The first of these, was the idea that by stopping the blow at a certain stage, before the carbon was all blown out, steel of desired quality could be obtained; the second, that of supposing that malleable iron could be made by burning out all the carbon by the blast.

All in the trade know, and have long known, that it

is practically impossible to stop the blow just at the right moment to leave behind a given quantity of carbon, and that this difficulty has been overcome by blowing until the flame contracts and alters its character; and when this occurs, the addition of the highly-carburetted spiegeleisen, in quantity regulated by its composition, supplies a proportion of carbon to the whole which admits of fairly accurate regulation.

But the impossibility of producing malleable iron by simply blowing out all, or what is supposed to be all, the carbon, is even now not nearly so well understood as it should be. I shall explain this presently, and show how the spiegeleisen, or ferro-manganese, overcomes this difficulty also. In my opinion this is the most important function of this compound, and one of great chemical interest. It is generally assumed that, if the blow could be stopped at the right moment—say, when 0·50 per cent. of carbon remained—that all would be well, and no ferro-manganese required. I find that this is a mistake—that steel thus made is worthless.

A good deal of discussion has taken place concerning the merit of Robert Mushet's contribution to the success of the Bessemer process, and some have evidently been deceived by confounding metallic manganese with the oxide of manganese, which commercially bears the name of 'manganese' only. It was, unquestionably, the oxide that Bessemer referred to in his early specifications, and not the metallic manganese of Mr. Mushet's 'triple compound.' As we shall presently see, this oxide of manganese cannot possibly do the work of the metallic manganese, the primary part of which work is effected in the act of its oxidation.

As already stated, the carbon and silicon contained in

the pig constitute the fuel which raises and maintains so remarkably the temperature of the molten metal in the Bessemer converter during the blow. This will be better understood by considering the quantities that are actually operating.

Supposing we have a charge of 6 tons of melted pig in the converter, this, according to the analyses already quoted, will contain an average of about 3 cwt. of silicon, for the complete combustion of which, or its conversion into silicic acid, 3½ cwt. of oxygen, or 14 cwt. of atmospheric air, is demanded. The carbon contained in the 6 tons amounts to 3·6 cwt., requiring for its combustion nearly half a ton of oxygen, or about 2½ tons of atmospheric air; altogether, 3 tons 4 cwt. of air.

The reader may estimate the volume of this himself, and understand thereby the necessity for the furious roaring of the blast which has to be injected to supply all this in the course of about 20 minutes. Much more is practically required, as the whole of the oxygen of the air is not combined.

Another striking indication of the power of the blast is displayed on examining the bottom of the converter. This is riddled with holes into which the finger may be thrust, and the great pool, the 6 or more tons (I have witnessed a blow of 15 tons) of liquid metal, stands over these holes without falling through them, is literally supported on air and air alone, the small density of the air being compensated by its great up-rushing velocity, which renders it impossible for the heavy metal to fall through. The metal is blown up faster than it can fall down. All this fuel, all this combustion is actually in contact with the metal in its midst, and hence is producing the maximum of possible effect.

A very interesting experiment might be made by using a specially prepared sample of pig-iron in which the quantities of carbon, silicon, sulphur, and phosphorus were equal—say 2 per cent. of each; running this into a converter, blowing for five minutes or thereabouts, then turning over, taking out a ladle sample; then putting on the blast, turning back, and blowing again for five minutes more; then taking another sample as before, and so on until the metal was ready for the addition of the spiegel or ferro-manganese.

We should thus, by analysing each of the ladle samples, learn the order of oxidation under these conditions of equal quantity. Judging merely from ordinary experience of the relative combustibility of the above-named, we should suppose that the phosphorus would be oxidised first, the sulphur second, then the carbon, and finally the silicon, though, respecting the latter, there might be some doubt, as we know so little of this substance in its free unoxidised state, in spite of the fact that its oxide, silicic acid, constitutes above one-half of the solid crust of the earth upon which we reside.

We should be taught by such an experiment that all such *a priori* speculative conclusions, based merely on considerations of the affinities of elements or compounds for each other when simply brought together without any chemical rivals, or other interfering agencies, are not reliable when the conditions are more complex.

To the best of my knowledge and belief, no such experiment as above described has yet been made, and therefore I will not attempt any solution of the problem in that particular form; but long ago, in the early days of the Bessemer process, I took samples from different stages of the blow in the manner described, but the pig-iron was

the ordinary commercial material, of which the composition has been already stated.

In this the sulphur and phosphorus were at a disadvantage owing to their very small quantities, but such being their condition in practical working, I will discuss the rationale of what actually occurs on this practical basis, adding that similar experiments to those made by myself have been subsequently made by many others with similar results.

The following are the results obtained in the course of one of my experiments which may be fairly selected as typical. The first column shows the percentage of carbon, silicon, sulphur, and phosphorus in the pig before melting; the second, after six minutes of blowing; third, after twelve minutes' blowing; fourth, when the blowing was finished.

	1	2	3	4
Combined carbon . . .	1·000	3·040	1·640	0·190
Graphite	2·570	trace	trace	trace
Silicon	2·260	0·955	0·470	trace
Sulphur	0·107	0·091	0·098	0·093
Phosphorus	0·073	0·070	0·070	0·070
Manganese	0·41	trace	trace	trace

Thus during the first six minutes all the graphitic carbon became combined and but little burned away, while nearly all the manganese disappeared and more than half of the silicon. In the second six minutes the silicon was again more than halved, and the carbon nearly halved; in the third six minutes about $\frac{8}{9}$ of the remaining carbon was burnt out, and nearly all the residue of the silicon, while throughout the whole time the sulphur and phosphorus

remained about the same, within the limits of error of an ordinary commercial analysis.

The first of these changes, viz. the conversion of the graphitic carbon to combined carbon, changed the soft granular grey pig (No. 1) into hard crystalline or 'white' iron—truly a steel, but too hard and brittle for practical use. This change has taken place in every case that has come under my notice, when grey graphitic pig-iron has been heated much above its melting-point. A good deal of disputation and theorising has been connected with this subject, of which anon, but in the meantime I merely state the results of my own experience. As will be seen by the figures, a small proportion of the carbon disappeared.

In other experiments, where the sample was drawn a minute or two earlier, this proportion was still smaller. The silicon in the same time was reduced to considerably less than half of its original amount, and the manganese all burnt away.

These quantities explain some of the visible phenomena of the blow. The magnitude and brilliancy of the flame is at first comparatively small. This corresponds with the fact that the combustion then going on is mainly that of silicon and manganese, but little of the chief flame-producer, carbon, being then concerned; but at the later stages, in which the carbon is the chief fuel, the flaming reaches its maximum.

But why should the manganese and silicon thus oxidise or burn before the carbon, and such highly-combustible substances as sulphur and phosphorus not burn at all?

There was a time when chemical text-books contained tables of chemical affinity, and substances were classed in the order of their affinities for oxygen or other elements

or compounds. Thus, the alkalis were the compounds having the strongest affinity for acids; next to these came the alkaline earths, then the basic oxides of the heavy metals, &c. This classification stands well enough where only one particular base and one acid are concerned, and all the other conditions, chemical and physical, are alike; but alter these, and the general statement of superior and inferior affinities tumbles to pieces.

To illustrate this, let us take a solution of the strongest of the alkalies, viz. caustic potash and a solution of baryta, which in such a table of affinities stands far below potash as a much weaker base. Having mixed these solutions, let us add a few drops of a sulphuric acid. According to the table and the general conception of relative basic energy or affinity for acids, the acid should combine with the stronger base, but such does not occur: it goes to the weaker, and throws down the familiar precipitate of baryta sulphate. But this is not all, for even when the potash has already combined with the sulphuric acid, this weaker base will tear the acid away from the stronger base, and take the acid to itself.

If this old theoretical order of affinities were not continuously violated by our water supplies, the inhabitants of all our cities, towns, and villages that are supplied by means of leaden pipes and cisterns would be slowly but certainly, and very painfully, poisoned. The oxide of lead (I speak in the old-fashioned language of acids and bases) is a weak base, weaker than lime, and very much weaker than soda or potash. If pure distilled water is allowed to stand over lead, a peculiar sort of solution and suspension occurs, rendering the water fatally poisonous if used as a daily beverage; but if a little sulphate of soda, sulphate of potash, or sulphate of lime be dissolved in the water, no

such poison is produced, for some of the sulphuric acid leaves these more powerful bases to go to the lead, and thereby coats the pipe or cistern with an insoluble varnish of lead sulphate, which saves our lives.

This may be very instructively demonstrated by putting a few shots into each of three bottles, half-filling one with distilled water, the second with ordinary hard water, and the third with the distilled water in which a little sulphate of soda or sulphate of potash has been dissolved. After some days' exposure, with occasional moderate agitation, test the water in each bottle by adding a few drops of weak solution of sulphide of ammonium. A blackening will indicate where the lead exists in solution or suspension. The bottles should not be corked, and the longer the water is left over and among the shots the more striking the experiment becomes.

Let us now suppose that we mix together solutions of various compounds of acids and bases, such as nitrate of silver with chloride of sodium, chloride of calcium with carbonate of ammonia, acetate of lead with chromate of potash, sulphate of copper with carbonate of soda, and so on with a multitude of examples that might be selected.

Will the compounds remain as before admixture, or, if they rearrange themselves, will it be in accordance with any order of *merely* chemical affinity? Clearly not. In the first example solid chloride of silver will be formed, in the second solid carbonate of lime, in the third solid chromate of lead, in the fourth solid carbonate of copper.

In every other case where a transfer of constituents can produce a solid compound, such transfer occurs, as though the physical attraction of cohesion altogether overpowers that of chemical affinity, or, at least, directs its operation.

Upon this general law are based the chief operations of modern chemical analysis.

Let us now apply this general law to the case of the silicon *versus* the carbon in the Bessemer converter. The selection of the oxygen is not merely determined by simple chemical affinity or mere chemical energy, but by this energy modified by the physical force of cohesion.

Silicon in combining with oxygen forms a solid flinty silicic acid; carbon forms gaseous carbonic oxide; therefore, in accordance with the law above illustrated, the oxygen goes first to the silicon.

But why should the highly combustible phosphorus and sulphur remain unaltered in the midst of all this vigorous combustion? It is doubtless due to the smallness of the quantities of these impurities. This influence of quantity I have already discussed in Chapter VII., when treating the theory of puddling.

The rapid disappearance of the manganese is, doubtless, due to its direct affinity for oxygen, aided by the fact that its oxide, when formed, is solid and readily combines with the silicic acid formed at the same moment by the oxidation of the silicon. Silicate of manganese is found in the Bessemer cinder.

I find that analyses made at Neuberg, in Styria, at a later date than mine, show a rather different result as regards the manganese. The original metal contained 3·460 of manganese; the first sample after blowing 1·645; the second 0·429; the third 0·113. But here was a very large proportion to begin with; the pig was from spathic ore, containing only 1·96 of silicon, and therefore not supplying, at the rate of combustion shown in either case, sufficient silicic acid to appropriate at once all the oxide of so much manganese.

I should add that such supply of material for forming such secondary compound when it thus occurs has been described as creating a 'predisposing affinity,' or heightening of the tendency of the original elements to combine. In my experiment the large relative supply of silicon predisposed the manganese to become oxidised. In the Styrian experiments this predisposing action was reversed; the excess of manganese stimulating the oxidation of the silicon, as shown by the result; in the first sample after blowing the quantity of silicon was then reduced from 1·960 to 0·443, to between a fourth and a fifth instead of to little less than half, as in mine.

Let us now consider the oxidation of the carbon and silicon in reference to the flame which roars from the mouth of the converter.

During the second six minutes the silicon and carbon are both reduced to about one-half, the carbon having the advantage of much larger quantity at starting, a great advantage seeing that the problem presented to the oxygen is that of getting at the impurity without attacking the iron itself. It will be easily understood that the smaller the proportion diffused among the iron the greater the difficulty of the oxygen to get at it.

This difficulty at last reaches a point at which it becomes insuperable, and when the silicon and carbon are no longer able to take all the oxygen to themselves, the iron, no longer protected thereby, begins to burn along with the remaining carbon, and the appearance of the flame is altered. This is the time when the converter is turned over, when, according to Sir Henry Roscoe, 'all at once the carbon lines disappear, and we get a continuous spectrum. The workman, by experience, has learned that this is the moment at which the air must

be shut off; but it is only by means of the spectroscope that this point can be exactly determined.' ('Spectrum Analysis,' p. 110.)

The spectroscope is a wonderful instrument, one of its great merits being remarkable docility. An energetic man like Sir Henry Roscoe, with a clearly defined theory before him, appears to be able to discover in a well-constructed spectroscope whatever the theory demands. The theory that prevailed at the date of Roscoe's Sheffield observations, described in his work on 'Spectrum Analysis' (1869), was that *all* the carbon is burnt out in the Bessemer converter, and that the carbon flame 'all at once' disappeared.[1] Subsequent analyses of the metal remaining at the end of the blow show that a notable quantity of carbon remains, combined with the remaining iron, and that particles of magnetic oxide of iron are mechanically intermingled (as explained in Chapter II.), the quantity of these depending upon how long the blow is continued after the alteration of the flame commences, the which alteration is very gradual, and does not accommodate

[1] Sir W. Roscoe's words are (p. 109): 'Those who are accustomed to work this process are able, by the simple inspection of the flame, to tell with more or less exactitude when the air has to be turned off. To those who are uninitiated in this peculiar appearance of the flame no difference at all can be detected at the point in which it is necessary to stop; but, by the help of the spectroscope, this point can be at once ascertained beyond shadow of doubt, and that which was previously dependent upon the quickness of a skilled eye has become a simple matter of exact and scientific observation.' Further on (p. 110), he states that: 'At a certain stage of the operation all at once the carbon lines disappear, and we get a continuous spectrum. The workman, by experience, has learned that this is the moment at which the air must be shut off, but it is only by means of the spectroscope that this point can be exactly determined.'

the above-named theory so correctly as the 'carbon lines' of the spectroscope.

I arrived on the field of Sir Henry Roscoe's spectroscope exploits shortly after him, and was eager to emulate his success in exactly determining the point at which the converter should be turned over (preliminary to shutting off the air). Although I used the instrument that was made for Sir Henry Roscoe, I only succeeded in determining the right moment for turning over by keeping both eyes open, and depending upon that which was *not* applied to the spectroscope.

Others have repeated this experience, and nobody has dared to practically rely on the spectroscope without the aid of the other eye. With large charges of metal it would be too costly a plaything.

There is no moment of sudden change, the starving out of the carbon and the burning of the iron proceed gradually, and the question to be determined by the director of the hydraulic machinery is how far this shall be allowed to proceed in order to obtain the best general result, or the special result required from a special blow. The change that actually does occur is not the extinction of the carbon flame, but the gradual superaddition of an iron-flame.

The theory of complete combustion of the carbon is logically supplemented by another concerning the use of the spiegeleisen, which is added after the blow. This theory assumes that the spiegeleisen simply supplies the carbon required for converting the iron into steel. It does this unquestionably, but it also does something more, and that something is very important.

As already stated, the metal at the end of a blow contains a measurable quantity of carbon, and more or less of black oxide of iron, due to the combustion of the metal.

In a fully blown or overblown sample these black particles are visible to the naked eye, when a fracture is made, after cooling.

What then happens when melted spiegeleisen or ferromanganese containing 5 per cent. or thereabouts of carbon is poured into the metal that has just been blown, and is lying stagnant on the side of the overturned converter?

Anybody who has watched the pool of metal from a suitable vantage-ground can answer this question as regards visible consequences. A violent ebullition commences immediately the highly carburetted metal is added.

What is the nature of this ebullition?

The answer to this question is supplied by the jets of flame that spurt out of the molten metal and the great blue flame which pours through the mouth of the converter, rising upwards with waving expansion and filling the surroundings with its weird and ghastly light. Carbonic oxide has been formed in the midst of the metal, and, on its issue therefrom, is combining with oxygen of the air to form carbonic acid.

What I have said concerning the little grains of black oxide of iron explains the source of the oxygen which must be somewhere and somehow within the molten metal, in order to supply the carbon of the spiegel with the necessary means for producing these effects.

In the early days of the Bessemer process the question of the homogeneity of the result was often raised, and the defects of certain samples were attributed to the deficient intermingling of the spiegel with the blown iron. It was, therefore, recommended that, after adding the spiegel, the converter should be turned again and blown for a few minutes, to effect a complete commingling.

George Brown, the able manager of the Bessemer department of the Atlas Works, maintained that this was unnecessary. I thought he was wrong, until he placed me on a platform where I could watch the result of repeated pourings of spiegel. Having seen this, and reflected thereon, I not only became a convert to George Brown's convictions, but was led to reflect on the rationale of this action, and to frame the above theory of the reaction of the particles of black oxide on the carbon of the spiegeleisen. At first I had to assume hypothetically the existence of the burnt iron. This led to further research, and the proving of the existence and composition of the black particles above described.

Everybody who has been responsibly concerned in Bessemer work is aware that the supply of carbon afforded by the spiegel or ferro-manganese is not always correct, according to the theory which states it to be simply divided between the metal of the converter and the spiegel itself. The spiegel may contain exactly 5 per cent. of carbon, and it may be added in the exact proportion of one to nineteen, and yet the resulting steel may sometimes contain more, sometimes less, than 0·50 per cent. of carbon. Hence the necessity for the laboratory carbon tests of every blow.

With the above in mind we may easily account for this. Suppose, firstly, that the blowing is carried so far that the quantity of carbon left behind in the converter charge is just enough to combine with all the oxygen of the little black grains for the production of carbonic oxide. In this case the amount of the carbon of the spiegeleisen which the oxygen of these grains removes will be just equal to that remaining unburnt in the converter charge, and nineteen parts of converter metal to one of 5 per cent.

spiegel will give just 0·50 per cent. in the product, *i.e.* the quantity that would satisfy the old theory.

Now let us suppose that the blowing has been carried a little farther than this. There will, of course, be more black oxide supplying more oxygen, and more of the spiegel carbon burnt than the converter iron can replace. The result will now be a milder steel, containing less than 0·50 per cent. of carbon.

On the other hand, if the charge be underblown, there will be more carbon than corresponds to the oxygen of the burnt iron, and, therefore, the excess of this will be added to the final result, and we shall have a steel containing more than the theoretical 0·50 per cent. of carbon. I have had to deal with cases in which nearly double the calculated quantity of carbon was found in the steel.

This view of the function of the carbon of the spiegeleisen greatly enhances the importance of the addition of Mr. Mushet's 'triple compound.' It not only supplies a measurable quantity of carbon, but operates as a reducing agent upon the mixture of metal and oxide. Any reader who questions the above explanations, and has the opportunity, should obtain a ladle sample of the best Bessemer metal at the end of the blow, and before the ferro-manganese is added. Let him then try to work it as malleable iron, which it should be if the blow merely removed all the carbon and the silicon. He will find that a fully-blown sample is not merely cold-short and hot-short, but is actually rotten.

I have thus tested an experimentally overblown sample that, in spite of overblowing, produced a high quality of mild steel after the addition of spiegeleisen, and found that the overblown metal, as it came from the converter before adding the spiegeleisen, crushed under the hammer like

sandstone. Ordinary fully blown metal is but little better.

While on this part of the subject, a word or two on the method of carbon determination devised by Eggertz, and so largely used in connection with the Bessemer process. It simply consists in dissolving a weighed quantity of borings from a sample ingot in a measured quantity of dilute nitric acid of standard strength, and maintaining this solution in a water-bath of standard temperature for a stated period. The solution is then allowed to cool, and is compared with a standard solution made, under the same conditions, from a piece of cast-steel of carefully-determined composition. The amount of dilution required to bring the solution under examination to the same tint as the standard solution determines the percentage of carbon.

Certain analytical chemists have made objections to this; have compared their own results obtained by this method with their own results obtained by more elaborate methods, and have found some discrepancy. This is not at all surprising, seeing that any novice may easily make mistakes, and any chemist, however skilful he may be otherwise, is a novice at this method until he has served a certain amount of apprenticeship to it. It demands a degree of special technical skill only obtainable by special practice, especially when the sample contains a trace of something (probably copper or nickel) which gives a masking green tinge to the solution.

I have superintended many thousands of these determinations, made by a specially skilled assistant, and yet, in many cases, have had to leave a blank in the laboratory report in consequence of both assistant and self being baffled by this green tinge.

Serious mistakes may be made by using an old standard

solution, or one that has been long exposed to the light. The standard solution should be renewed weekly, or oftener, and kept in the dark.

With such precautions, and the practical skill easily obtainable by first working with an expert, and comparing results obtained from the same samples, the calorimetric process of Eggertz is sufficiently accurate for commercial purposes. The errors may be kept well within $\frac{1}{20}$ per cent. of double range—*i.e.*, supposing the dilution reads to 0·475 in a given sample, we may safely conclude that its exact proportion of carbon is not less than 0·45, nor more than 0·50 per cent.

As a skilful assistant can easily make fifty or sixty carbon determinations in a short day by this method, its practical value is evident where the result of every blow requires determination.

But in order to be secure, the chemical carbon test should be supplemented by mechanical bending tests, and these compared. When they are at variance, as when the bending test indicates greater hardness and brittleness than is due to the percentage of carbon shown by the laboratory report, the pig and the ferro-manganese should be chemically overhauled, as one or the other probably contains a mischievous quantity of phosphorus. By determining the percentage of phosphorus in certain parcels of hematite pigs delivered for Bessemer work, and comparing with these determinations the relation between the bending and carbon tests of the steel made from such iron, I have found that, as the phosphorus increased, the hardness of the steel, in relation to its percentage of carbon, increased proportionately, and *vice versa*; when the pig was exceptionally free from phosphorus, the steel was softer than its percentage carbon indicated.

In the course of these investigations, an exceptionally fine sample of Cleator pig (as regards phosphorus impurity) was delivered. When I had ascertained its composition, George Brown, at my suggestion, added to one blow an exceptionally large quantity of spiegeleisen, thus obtaining a percentage of carbon equal to that of ordinary pot-steel. It proved to be sound, and was really a fair sample of tool-steel.

On the basis of this result I made a suggestion in 'Iron' some years ago, which I now repeat with increased confidence—viz., that a very lucrative and useful business is open to anyone practically skilful in Bessemer work, who will erect a small-sized Bessemer plant, and work with very carefully selected charcoal iron, for the purpose of making high-class steel. I am convinced that the question of whether such steel shall be equal or inferior to crucible steel, simply depends upon the purity of the material from which it is made. In the absence of phosphorus, no basic lining would be demanded.[1]

The theory of the basic process is simple. The problem is to take out the sulphur and phosphorus from inferior raw material to such an extent that the result shall be equal to that obtained from costly selected hematite pig iron—nearly free from phosphorus.

As already explained, a given chemical combination is greatly encouraged when the result of the compound has something to combine with immediately it is formed; thus

[1] To render this more intelligible to those who have not been practically engaged in Bessemer work, I should explain that while good pot-steel may contain above 2 per cent. of carbon, ordinary Bessemer steel will not bear more than about $\frac{3}{4}$ or at the most 1 per cent. of carbon without becoming worthlessly brittle. This I attribute to the phosphorus. The exceptional sample above referred to carried safely $1\frac{3}{4}$ per cent.

sulphur and phosphorus, when they combine with oxygen, form acids, and these acids combine with bases; therefore, if a base is within chemical reach, the oxygen is encouraged thereby to go into acid-forming combination with the sulphur or phosphorus.

Otherwise stated, and perhaps more correctly, we may have two bodies—A and B—capable of combining, but the circumstances are unfavourable. Now add a third—C—capable of combining so as to form a triplex body; this third will aid the combination of the other two. In this case A represents either sulphur or phosphorus, B oxygen, and C the lime or magnesia of the basic lining. A and B together, but not separately, combine readily with C if it is at hand; and thus the presence of C acts by the predisposing affinity already described. Ordinary linings contain a predominating amount of silicic acid, which, of course, affords no encouragement to the acid-forming combinations of sulphur and phosphorus with oxygen; while the basic lining presents lime and magnesia, with which these compounds so readily combine.

CHAPTER XVII

MANGANESE AS A STEEL-IMPROVER

THE reader may, possibly, have concluded ere this that I have said quite enough about the stubbornness with which the last portions of mischievous impurities are retained in iron, in spite of the Bessemer blast and other oxidising agencies; but I have not quite done with the subject yet. The principle of quantity, as affecting chemical affinity, applies, in like manner, to the last traces of the silicon; I may, perhaps, venture to say, most especially to silicon.

For reasons already explained, pure iron is commercially unobtainable. Even though it be made from ores containing neither sulphur nor phosphorus, and with pure charcoal fuel, we cannot get rid of the last traces of carbon. The iron itself begins to burn when raised only to a welding-heat, unless it contains a small protecting proportion of carbon to take up the presented oxygen. This small quantity of carbon lowers its melting-point, and renders its fusion possible, which would not be practically the case if the iron were pure. If such iron were heated in an ordinary crucible, however well protected from the atmosphere, it would attack the crucible itself, before reaching its melting-point, by combining with its silicon. If the crucible be 'brasqued,' the iron is presented to carbon. If a crucible of refractory lime, or magnesia, or alumina were used, the result would, probably, be a reduc-

tion of some small proportion of these oxides by the iron, and its combination with the calcium, magnesium, or aluminium.

We may now ask, What becomes of the last traces of the silicon in the Bessemer process? If they are not burnt out, where are they? Do they remain in the product? and, if so, what effect have they on its quality? These questions bring us at once to the remaining unconsidered element concerned in the Bessemer process, viz., the manganese.

There can be no doubt that manganese is a benefactor to steel—both to Bessemer steel and to the best old-fashioned cast steel. It has been supposed that it forms an alloy, and improves the steel thereby; but this is disproved by the analysis of the best steel, which shows the absence of manganese; and, further, by the fact that the presence of manganese in the finished steel is prejudicial. It is evident that the manganese acts as a purgative of some sort in the course of the manufacture of steel, and that its final excretion is a necessary condition of its beneficial action.

My attention was specially directed to this subject, about twenty years ago, while experimenting upon an invention that I subsequently patented (No. 4, January 1, 1869), which consisted in adding oxide of manganese to the ordinary fettling of a puddling-furnace; this oxide, when heated, giving off its oxygen to the melted pig with which the furnace was directly charged; and the manganese, when reduced by the carbon of the pig, was to be added to iron or puddled steel, and thereby improve it. This expectation was based on the above-named alloy theory, which I, in common with others, then supposed to be sound.

It turned out, practically, that the iron produced with the aid of this fettling was not improved to any notable extent. It was more uniform in structure, less fibrous than iron wrought in the usual way from the same pig. But the puddled steel was decidedly improved—so much so, that the invention would have been very valuable had the demand for puddled steel not been superseded by the Bessemer process.

The puddled ball as it came from the furnace contained a notable amount of manganese; when hammered, it contained less; when rolled, less still; when re-heated, piled, and finished, none, or only a trace. Thus it appeared that the manganese passed out in the working; but more carbon remained in the puddled steel thus produced than in similarly treated samples wrought without the manganese fettling.

The steel was harder, closer, and better in all respects; the fracture finer, and more like cast steel; the iron was rather too steely for iron, but otherwise good.

An examination of the hammer-slag, and the droppings of fused cinder from the re-heated metal on its way to the rolls, revealed a solution of the mystery. They contained a considerable, but very variable, quantity of silicate of manganese. It was evident from this, that the manganese must have combined with the silicon still remaining after the iron or steel was puddled.

This at once suggests a theory of the purgative action of manganese—viz., that its beneficial influence is due to its removal of the last adhering traces of silicon—a very important act of purification in the case of steel, seeing that silicon seriously increases the hardness and brittleness of steel. The best steel, as already explained, is that which is composed of the purest iron, with nothing else but the purest carbon in combination.

The well-known fact that black oxide of manganese improves the quality of pot-steel, when added according to Heath's process to the contents of the crucible, confirms this view of the action of the manganese, as there rises to the surface of the steel in the crucible a crust of cinder chiefly composed of silicate of manganese, with probably a small quantity of the silica of the melting-pot itself, which otherwise would be liable to contaminate the steel. When the spiegeleisen, or ferro-manganese, is poured into the Bessemer converter, a similar uprising of manganiferous cinder occurs.

But in the case of the puddled bar which parted with its manganese after the puddling was finished, and the Bessemer metal which throws up its silicate of manganese after the blow is ended, the siliceous compound is not merely due to the combination of simple silicon with simple manganese; it is oxide of silicon with oxide of manganese. Whence comes the oxygen in these cases?

This question has long been a puzzle. Mr. R. Mushet has suggested that it is obtained from occluded oxygen. Since my discovery of the grains of black oxide in the burnt iron (see Chapter XIV.), and finding them again in the samples of Bessemer metal taken from the converter before adding the spiegeleisen, I have concluded that the supply is derived from these, on their reduction to good metal.

I agree with Mr. Mushet that the oxygen is there; that it is *included*, in combination as oxide, but not in assuming that it is *occluded* as simple gas.

It is well known that some gases are, under certain conditions, thus occluded, and condensed within iron. Hydrogen, carbonic oxide, carbonic acid, nitrogen, were extracted from horseshoe nails and from meteoric iron by

Graham (see Chapter XXI.); but neither Graham nor any other chemist has found free, uncombined oxygen in any kind of iron.

A little reflection will show that its *retention* is chemically impossible. If it got there for a moment, it would combine with the heated iron, or with the carbon, or with the carbonic oxide, according to circumstances. In combining with the iron, the black, magnetic oxide would be produced.

A momentary occlusion of oxygen, followed by combination with iron, and the formation thereby of the black grains, may probably occur. I say 'probably,' because an explanation is thus afforded of the fact that the black grains of the burnt iron are not merely superficial, but are found deep within its substance. They were thus within the burnt armour-plate where I first found them, and in the armour-plates that were overdone in re-heating (see Chapter XIII.). In both these cases, and in all ordinary instances of 'burnt iron,' there is internal oxidation, without fusion having occurred.

The theory of the action of manganese expounded above assigns to that metal a twofold function—first, that of co-operating with the carbon in reducing the iron oxide, which weakens the cohesion of the metal; and second, that of removing the last traces of silicon, which imparts a glassy brittleness, especially when combined as a silicate.

I even venture to suspect that it has a third function—that the fusible silicate thus formed internally in the midst of the fluid metal performs some amount of washing out of sulphur and phosphorus, supplementary to that which occurs in puddling. I have not proved this by analyses of the cinder, and it may be difficult to prove, as the quantity must be very small; but if even a trace of

phosphorus exists there, its removal must appreciably improve the quality of the steel.

To understand clearly why manganese is specially adapted for these actions, we must examine its peculiar relations to oxygen. Many metals form a series of oxygen compounds, the higher oxides more or less readily parting with some of their oxygen, the lower oxides hungering for more. Manganese is an exaggerated example of this. There is the protoxide, or manganous oxide (MnO), a powerful base; the sesquioxide, or manganic oxide (Mn_2O_3), a feeble base; there is the red mangano-manganic oxide, a compound of MnO with Mn_2O_3, which is neither basic nor acid, but neutral; there is the well-known commercial black oxide, or dioxide (MnO_2), also neutral; and there are the acid oxides, manganic acid (MnO_3) and permanganic acid (Mn_2O_7).

The members of this family group are curiously addicted to transformation, the lower oxides, when in presence of redundant oxygen, becoming more highly oxidised, and the higher oxides giving up their excess of oxygen to any neighbouring substance that may be in want of it, even to its manganous brethren. Every tyro in chemistry knows that by simply heating the black oxide a supply of oxygen gas may be obtained, one-third of its oxygen being given off, and the red oxide left behind; and that, if the black oxide is heated with sulphuric acid, one-half of the oxygen is given off, leaving the protoxide to combine with the sulphuric acid.

So remarkable are these shiftings of oxygen, that the compound obtained by fusing together caustic potash and the black oxide received long ago the name of *mineral chameleon*. The manganate thus formed gives a green solution with a little water; with more water, a claret-

coloured solution, having taken up more oxygen and become permanganate. This, again, if brought in contact with organic matter, gives up this excess of oxygen, and then still more, passing down from the red to the green manganate and thence to the lower oxides.

Such a free giver and free taker of oxygen, when in the midst of such materials as we have in the newly-blown Bessemer metal, is just what is required to take out the damaging oxygen, or to oxidise the silicon. My theory is that it does both—takes oxygen from those black grains of magnetic oxide of iron, becoming thereby red oxide of manganese (mangano-manganic oxide); then, on meeting with the silicon, reduces itself to a basic oxide, by giving up more oxygen to the silicon, which silicon, thereby converted into silicic acid, combines with the basic oxide of manganese, and forms the silicate of manganese found in the cinder.

In the case of the Bessemer metal, the deoxidation is aided by the carbon of the spiegeleisen, when this is used. The greater portion of manganese in ferro-manganese renders less carbon necessary, as the manganese may do all this part of the work.

The rationale of the action of the black oxide of manganese added to the crucibles in the manufacture of Sheffield pot-steel is essentially the same, though somewhat modified. Here we have none of those black granules of magnetic oxide of iron demanding reduction by *metallic* manganese, but we have (as proved by the analysis of blister steel) a residuum of silicon to be oxidised, combined, and removed. For this work we require the *oxide* of manganese, and such an oxide as can readily give off enough oxygen to convert the silicon into silicic acid.

This is afforded by the black oxide, which by simple

heating gives off one-third of its oxygen, and becomes red oxide; this, when presented to an acid, gives up more, and becomes basic monoxide, which combines with the acid: thus, the first evolution of oxygen acidifies a portion of the silicon to silica; this combines with its equivalent of basic oxide of manganese, in doing which it acidifies some more silicon; and so on throughout.

In reference to the existence of stubbornly-remaining traces of silicon in iron and steel, I should explain that chemical analysis is less effective in separating and weighing very small quantities of silicon than of sulphur, phosphorus, or carbon. If there be any sulphur, we can oxidise it, and thus obtain a solution of sulphuric acid in water. By adding to this a few drops of solution of barium chloride, a dense, white, insoluble precipitate of the sulphate of baryta is thrown down, in a form that can easily be separated, dried, and weighed. This dried sulphate contains but $\frac{1}{11}$th of its weight of sulphur; therefore, $\frac{1}{11}$th of a grain of sulphur in this compound is weighed as one grain; and $\frac{1}{1100}$th part of a grain is weighed as $\frac{1}{100}$th of a grain. But in the analytical determination of silicon we have to weigh it as silica, which is composed, in round numbers, of $\frac{1}{2}$ silicon and $\frac{1}{2}$ oxygen: and, therefore, when we approach the limits of weighable quantity of precipitate, the quantity of silicon is five and a half times greater than of sulphur; or, otherwise stated, the delicacy of detection and determination of sulphur is five and a half times greater than that of silicon.

The determination of the phosphorus by the molybdate method (see Chapter XII., page 224) is still more delicate than that of sulphur. Here the precipitate that is weighed is sixty times heavier than the phosphorus it contains, and

therefore our smallest weighable quantity of silicon is thirty times greater than that of phosphorus.

There is another element of difficulty and uncertainty in the estimation by analysis of small proportions of silicon. It is that silica may exist in two conditions—the soluble, or colloidal, and the insoluble. While engaged as chemist in the works of Sir John Brown & Co., it was on several occasions my duty to watch the working of experimental samples of iron (puddled bar) that had been analysed by reliable chemists, and reported to contain mere traces of silicon, and similar samples in which I had also failed to separate weighable quantities of silica. Nevertheless, from this iron, when piled, and re-heated, and hammered, there was squeezed a notable amount of fusible cinder, in which I found weighable quantities of silica.

In ordinary steel-melting, where a sample supposed to be free from silicon is melted in a crucible with oxide of manganese, there arises a scum of cinder containing silicate of manganese and silicate of iron. It is true that some of the silica in this case may be supplied by the pot itself; but putting this common experience by the side of that described above, leads me to suspect that in our analyses we have missed some of the silica, owing to its solution in the acid used for dissolving the iron. In carefully-checked analyses there is usually some 'loss,' and this may account for it. I do not assert that this is proved, but suggest its probability, as a subject for further research.

Some investigations have lately been made by Mr. Hadfield, with curious and interesting results. He agrees with myself and others in attributing brittle hardening to small proportions of manganese in steel, and states, in his Paper read before the Institution of Civil Engineers, February 28, 1888, that 'the maximum amount that may

be present in the low-percentage manganese steel, before the steel becomes absolutely brittle and rotten, seems to be 2½ per cent.' At higher percentages, Mr. Hadfield says, 'the brittleness cannot be too strongly emphasised; in fact, it seems to partake more of the nature of glass, or other similar substances, than of a metal such as steel, if this term can be applied.' Thus, a bar-casting containing 4·73 per cent. of manganese broke into three pieces on being dropped on an iron floor from a height of 3 to 4 feet; and another specimen, containing 0·48 per cent. of carbon and 4·9 of manganese, 'though exceedingly ductile when hot, in the cast state, when cold, could be reduced by a hand hammer to a fine powder, no cohesion seeming to exist between the particles.'

Mr. Hadfield's experiments show that the maximum of such brittleness is reached at between 4 and 5 per cent. of manganese, 'and after this a slight increase of strength takes place'; and this goes on until at about 7½ per cent. a totally different material is obtained—a material to which Mr. Hadfield has given the name of 'manganese-steel,' a name which I regard as misapplied and unfortunate, as it is evidently an *alloy* of iron and manganese, although the manganese obstinately carries a certain amount of carbon with it.

That it is an alloy (which Mr. Hadfield admits, in spite of the name he applies) is evident from the change of properties which the manganese effects, the most remarkable of which is the destruction or obliteration of the magnetic properties of the iron. As every mathematical-instrument maker knows to his cost, the smallest particle of iron in the brass or bell-metal of a theodolite, or other instrument in which a compass-needle is included, is ruinous by its disturbance of the needle; and, there-

fore, every casting for such an instrument has to be carefully 'tried,' by presenting all parts of its surface to a well-poised magnetic needle.

But this 'manganese-steel,' when the proportion of manganese reaches 8 per cent., loses all but the faintest trace of magnetic properties. Again quoting Mr. Hadfield's Paper: 'Dr. Hopkinson, who has carefully dealt with this subject, finds that, in a substance with a substantial proportion of manganese, the latter annihilates the magnetic property of iron; and steel containing 12 per cent. of manganese is practically non-magnetic.' A small piece of wire containing 0·85 per cent. carbon and 13·75 per cent. manganese 'was not attracted in the slightest degree by the most powerful electro-magnet, capable of lifting a ton.'

The alteration of mechanical properties is well illustrated by the history of this piece of wire (No. 19, Birmingham wire-gauge). Mr. Hadfield tells us that he 'first attempted to draw direct from the rods, but with little progress, the wire, owing to its hardness, breaking into short lengths when pulled through the wortles. Ordinary annealing was tried, but with no better results. As exceedingly good bending tests had been obtained with bars from the same steel, when heated to a yellow heat, and plunged into cold water, the rods were treated in the same manner. These were coiled up, heated to whiteness, and plunged into cold water. The material was then easily drawn; but after every reduction through two sizes its ductility was again lost, and the operation of heating to whiteness and quenching in cold water was again necessary.'

A sample of this wire which had been thus treated five times, was exhibited at the Meeting. In its hard

state it bore a tensile strain of 100 tons to the square inch in the experiments of Professor Barrett. A similar result was obtained by the manager of the wire department at the Barrow Steel Works, who reported 'that it would stand any tensile strain up to 100 tons to the square inch, according to temper, and the elongation was extraordinary.'

I state these particulars to prevent misunderstanding. What I have said above concerning my own view of the functions of manganese in steel-making is not affected by these results, which clearly point to the existence of a true alloy, which is quite different from steel in which a small percentage of manganese is introduced as a foreign substance. I may further add, that I have made no experiment on this alloy myself, and state the above entirely on the authority of Mr. Hadfield's Paper, a copy of which he kindly sent to me.

I fully agree with Mr. R. Mushet, who, writing to Mr. Hadfield on this subject, said: 'Your material is really not steel, but an alloy in certain proportions of iron and metallic manganese, containing also carbon, but as little of that as you can help. Your alloy possesses some of the properties of steel, and it is to a certain extent a substitute for steel, just as brass, which is not copper, is, nevertheless, a substitute for copper.

The reader will naturally ask, why steel itself is not described as an alloy of iron with carbon, seeing that its melting-point and other properties are so different from those of either the iron or the carbon. The ordinary answer to this is, that an alloy is a mixture or combination of two metals, but carbon is not a metal. In the following chapter another answer is supplied.

Before leaving this subject of manganese, it is only fair

to add that the view expressed at the commencement of this chapter, concerning the mischievous action of small proportions of manganese in iron and steel, is disputed by many metallurgists, whose authority I should be the last to disparage.

Reviewing the subject all round, it is very embarrassing to the student to find such discrepancies among those to whom he looks for guidance.

Is he to disregard their positive assertions relative to the excellence of certain samples said to contain 1 to 2 per cent. of manganese, and the elaborate tables of tenacity, elongation, reduction of area, &c., by which they are supported? I cannot advise him to do so, but warn him to guard himself against practical conclusions based on all gradually-applied strains *only*. The reasons for this are detailed in Chapters XI. and XII.

This warning applies generally; but, in the case of the asserted improvement of steel by small additions of manganese, there is another source of fallacy that is specially connected with this substance, and which I suspect is at the bottom of the discrepancies referred to above.

As stated in the beginning of this chapter, I discovered that my own child—the patent manganiferous iron—was, chemically speaking, a wayward bairn; that in its infancy, as puddled bloom, it dutifully obeyed me by taking up and adhering to the manganese I desired it to retain. But as it advanced in life it treated the manganese as bad children treat parental precepts, gradually dropping it at every stage of growth—at its hammering, rolling, re-heating, piling, &c., until all had gone.

Now, had I not detected this—as I certainly should not had I only examined samples in the laboratory testing-room—I should have declared that the finished samples

contained as much as 1, 2, and in some cases even more than 2 per cent. of the supposed improver. These samples, being of remarkably good quality, my natural inference would have been that their excellence was due to the presence of the improver.

The circumstances that first led me to suspect the contrary—viz., that it was the absence rather than the presence that did the improving—were that the cinder in the puddling-furnace was very fluid, and that in every stage of the working an unusually large amount of cinder came out of this manganiferous iron and steel. The quantity that trickled down from the puddled ball as it was run, on the lorry, to the steam-hammer, was unusually large; the quantity squeezed out from the spongy ball under the hammer was unusually large, and the ball itself unusually tender—it required much 'humouring,' or it would have splashed away from the block; the quantity that ran from the faggots of the pile in the re-heating furnace, and that trickled down from the lorry as this pile was carried to the rolls, and the quantity squeezed out by the rolls, even in the last stage of completing the boiler-plate that was first made, and tested mechanically, all suggested a measurable alteration of composition, and led me to make analyses of the same bloom at different stages of working—analyses that revealed the remarkable fact that, in its most highly-worked condition—viz., that of sheets and wire—my patent manganiferous iron and steel contained no manganese at all, but was excellent material, standing every kind of bending, flanging, and punching tests, ram's-horn, holeing, and other fancy tests, besides drop-tests and the ordinary extension tests, with only moderate tenacity. It was, in short, remarkably tough and soft when the manganese was all gone, though somewhat steely in its

hardness in the earlier stages, while the manganese remained.

The question obviously suggested by these facts is, whether the analyses upon which so many have based their conclusions respecting the improving action of manganese were made before or after the steel was worked. If made, as is commonly the case, upon borings from the ingot before working, we may be pretty certain that the steel supposed to be so greatly benefited by the alleged percentage of contained manganese, contained no such percentage, or only a trace, or even none.

Worse still than this are the cases where the percentage-proportion of manganese has been determined synthetically, according to the quantity added in the form of spiegeleisen, or ferro-manganese. It is commonly assumed that, if you add, in this manner, two parts of manganese to ninety-eight parts of molten iron and steel, and then run this into ingots, and work it up, that the final product will contain 2 per cent. of manganese. The fallacy of this purely mathematical conclusion is obvious from what I have explained above.

CHAPTER XVIII

A THEORY OF STEEL

THE following is the first of a series of Articles that I contributed to 'The Metallurgical Review,' published by David Williams, New York, 1878. I reprint it with no further alteration than the omission of some paragraphs relating to cementation, the substance of which is included in Chapter XV.:—

'The most important physical discovery ever made by man was that of a substance which is so hard that it can cut or otherwise shape almost every other substance on the face of the earth, and yet may be so modified in hardness that it may cut and shape itself. It thus may be formed into any kind of tool or instrument that human wants and human ingenuity may suggest and devise.

'The bronze of the ancients partly supplied these requirements, but in steel we have their complete fulfilment. Some idea of the vast utility of steel may be formed by picturing to the mind the condition to which we should be reduced if deprived of it altogether. The progress of prehistoric man may well be divided into the three leading epochs of the Stone, the Bronze, and the Iron Ages, for they mark the boundaries of differences of condition almost amounting to what might result from a variation of species.

'The leading property of steel, upon which its bene-

ficence to man mainly depends, is, to coin a convenient word (which I venture to do in this instance), its *temperability*. By heating and cooling it in different degrees, and at different rates of rapidity, we may not only obtain a great difference between extremes of hardness and softness, but any intermediate degree of hardness and softness between these extremes.

'Why is this? Upon what depends this wondrous and incalculably useful property? We know that it is conferred upon iron by the addition of 1 per cent., or thereabouts, of carbon; but why should this trifling quantity of carbon, having no such property itself, confer this property on iron? Here is a question involving the philosophy of one of the most useful attributes of any form of inorganic matter.

'My object in the present Paper is to offer a contribution towards the solution of this very interesting problem.

'A chemical compound is a substance formed by the union of different substances in definite and invariable proportions. Its properties commonly differ very materially from those of its constituents; and, when solid, it is usually capable of assuming a definite crystalline form. In a mechanical mixture the constituents may be blended in any proportions, and the mixture displays more or less distinctly the properties of both as diffused between each other. Generally speaking, the properties of the mixture are intermediate between those of its constituents; but there are some exceptions to this.

'To which of these is steel to be referred? Is it a chemical compound of iron with carbon, or a simple mechanical mixture?

'That it is not a chemical compound, properly so called, is settled by the fact that we have steel containing

any proportion of carbon between the ¼ per cent. of the mild steel, or homogeneous metal, now so largely produced by the Bessemer, Siemens-Martin, and other processes, up to the hardest draw-plate steel, containing 3 per cent. of carbon.

'On the other hand, the special properties of steel are not at all intermediate between those of iron and carbon. If the iron were simply hardened, we might maintain that the properties of the diamond were imposed upon the iron by the carbon admixture. But this is not all: its hardness may be modified by simple heating and cooling, and, besides this property of temperability, the iron has acquired a remarkable increase of fusibility. This property is given by the addition of a very small proportion of a substance which is infusible by any means at present within human reach.

'What, then, is steel? My reply to this question is that it is an alloy of metallic iron with a definite chemical compound of iron and carbon that has metallic properties. This definite compound I suppose to have a composition corresponding to the formula Fe_4C. The existence of such a definite carbide of iron has been accepted by some metallurgical chemists, and disputed by others. The evidence afforded by experiments made with the object of forming it directly by fusing iron in contact with carbon, is certainly very unsatisfactory; but in this case, as in many others, it happens that what we are unable to produce by direct effort is indirectly or accidentally prepared for us.

'In the Swedish and German spiegeleisen, so largely used in the manufacture of Bessemer steel, we have the largest proportion of combined carbon that is to be found in any kind of cast iron. We also have in this a most re-

markable development of crystalline structure, indicating definite chemical combination. Mere mechanical mixtures do not crystallise.

'But there are great differences in the qualities of different brands or samples of spiegeleisen, and also great differences in the completeness of the development of its crystalline structure.

'When I was engaged in the laboratory of the iron and steel works of Sir John Brown & Co., of Sheffield (this was before the recently-invented "ferro-manganese" was used), it was my duty to analyse the various samples and deliveries of spiegeleisen, in order to determine their richness in carbon and manganese, and their degrees of freedom from such impurities as phosphorus and sulphur.

'I soon discovered that the best qualities were those which exhibited the most fully-developed crystalline structure—those which fractured into the most brilliant definite and angular plates, or laminæ. This crystalline structure reached its maximum development in curious patches of honeycomb structure occurring in the best samples, and produced by the metal crystallising completely into distinct, separated plates, which stood up edgewise, and crossed each other at intervals of about $\frac{1}{4}$ to $\frac{1}{2}$ inch apart. These plates were but little thicker than stout card. I analysed several, and found them richer than ordinary samples, or the average of the sample in which they occurred, both in carbon and manganese; and, further, that the proportion of carbon was remarkably uniform, the difference being no greater than was fairly due to the errors of ordinary commercial analysis.

'The following is the average result; calcium, copper, and other minute impurities, not determined:—

Iron	84·46
Combined Carbon . . .	4·48 to 4·50
Graphitic Carbon, &c.	0·40
Silicon	0·80
Phosphorus	0·04
Sulphur	0·10
Manganese	9·21

'I had no theoretical object in view when making these analyses. The crystals were selected as affording a standard of commercial excellence to which all samples should be referred, and judged according to their approximation.

'These analyses were made in 1869, and it was not until more than two years afterwards that the idea of calculating the percentage of carbon upon the iron, and comparing the results with the formula of Fe_4C, suggested itself.

'At first glance they appeared to contradict the idea of such a composition which demands more than 5 per cent. of combined carbon; but a moment's reflection showed that the quantity to be taken into account was not the percentage of the carbon in the whole of the spiegeleisen, but that in the iron it contained. Working this out, the above figures give, upon every 100 parts of iron in the compound, 5·33 of carbon. The quantity theoretically demanded is 5·36, or, more accurately, 5·357.

'The analyses sent from Germany with some of the finest samples of spiegeleisen generally give a higher percentage than this—one I have now before me amounts to 5·73 per 100 of iron; but in this the total carbon is stated, including the graphitic, or uncombined, which should not be included in this theoretical calculation.

'The idea of seeking for this definite compound in spiegeleisen is not a new one, as may be seen by reference to Dr. Percy's "Metallurgy of Iron and Steel," page 118,

where he justly complains of the ignoring of the manganese in these calculations, which are given as percentages of the spiegeleisen, instead of on the iron it contains. Thus he says: "In the tabular list of analyses of specular cast iron in Kerl's handbook, there are three by Karsten in which the chemically-combined carbon ranges from 4·121 per cent. to 5·111 per cent.; and in these there is no allusion to the presence of even a trace of manganese; yet in Karsten's own record of these analyses it is expressly stated that manganese was not sought for."

'The discrepancies in these analyses to which Dr. Percy alludes are sufficiently explained in my own experiences, as I found the quantity of combined carbon in ordinary samples, representing the bulk of different casts of spiegeleisen, to vary from 3·11 to 4·50 per cent. of the whole. All of these were sufficiently crystalline to be described as fair specimens of specular cast iron.

'The constancy of composition and maximum proportion of carbon above described were only found when I carefully selected the thin plates forming the walls of the honeycombed cavities. The chemists quoted by Dr. Percy appear to have simply examined the ordinary bulk of good samples of specular iron. Assuming this, their results correspond closely enough with mine.

'I now come to the bearing of this upon the main question of the temperability of steel.

'In the first place, it must be noted that steel is always more fusible than malleable iron; that this fusibility increases with an increasing proportion of carbon; that spiegeleisen is still more fusible than any weldable steel; and that, as Gmelin says, it "cannot be welded, because it becomes pasty at the very lowest welding-heat" ("Handbook of Chemistry," vol. v., page 211, Cavendish

Society's Edition). The greater the proportion of carbon in the spiegeleisen, or other white pig iron, the lower is its fusing-point, other constituents remaining the same.

'We may, therefore, conclude that the compound Fe_4C is more fusible than steel, and far more so than iron. It is now well known that malleable or nearly pure iron, which of itself is not fusible in an ordinary furnace, may be easily fused, at a temperature far below its own naked fusing-point, by immersing it in a bath of spiegeleisen or other pig iron containing much combined carbon. In like manner, iron is fusible or soluble in melted Fe_4C.

'We thus reach the propositions:—(1) That iron and carbon may, and do, unite and form a definite chemical compound having a composition corresponding to the formula Fe_4C; (2) That this compound is more fusible than steel, and much more fusible than iron; (3) That iron is fusible, or, I may say, soluble, in melted Fe_4C.

'If these propositions be accepted, a very small step carries us at once to my theoretical assumption concerning the constitution of steel—viz., that it is iron dissolved in, or alloyed with, the metallic or pseudo-metallic compound Fe_4C.

'The modern manufacture of homogeneous steel supplies us with direct evidence of this view, inasmuch as steel is now actually made on a large scale by fusing scrap iron in a bath of melted spiegeleisen.

'At first sight, the old method of making steel by cementation appears to present a difficulty, inasmuch as steel is here made by simply exposing red-hot iron to the direct action of carbon; but we must remember that this cementation is a mystery and a difficulty under any hypothesis. A little reflection will show that the theory of the constitution of steel above expounded supplies a

very simple solution of this stubborn, old-standing, physical conundrum.

'If we take two metals that vary considerably in their fusing-points, and yet are capable of forming alloys with each other, we may effect a union between them by melting the more fusible, and bringing the less fusible, while still solid, in contact with the liquid metal. The process of tinning, and the so-called "galvanising" of iron, show this. If a plate of clean copper be immersed in a bath of melted tin, a film of tin will adhere to its surface; if the immersion is continued, the tin gradually penetrates the copper—"soaks" into it—and in time will penetrate to the middle of a thick plate or bar. The same occurs with iron, whether the bath be tin or zinc. It is not even necessary to have a bath of tin, for, if the melted tin be simply brushed over the surface, and the heat maintained, it will penetrate or soak into the substance of the solid metal more or less completely, according to the time and temperature. This kind of action is displayed most strikingly by mercury.

'In the cementing-furnace we have a temperature at which Fe_4C becomes, if not fluid, at least pasty, and all that we need to assume is that it is directly formed by the direct contact of the outer surface of the bars with the "cement powder," or carbonaceous matter packed between them, and that, when formed, it acts in the same manner as a pasty film of barely-fused tin is known to act on copper, iron, &c., or as mercury acts upon any of the metals with which it is capable of amalgamation.

'Cementation thus regarded is strictly analogous to the amalgamation or the "soaking" of a more into a less fusible metal, forming thereby an imperfect or irregular alloy. Blister steel is an imperfect or irregular steel, of but little value, unless rendered completely homogeneous

by fusion, or partially so by shearing, faggoting, and tilting.

'We may now venture to grapple with the question stated at the onset, viz., What is the cause of the temperability of steel—upon what physical condition does it depend?

'I am not one of those physical anatomists who imagine that, by means of the mathematical scalpel, they can lay bare the molecular structure of inorganic matter, measure the dimensions of its atoms, and describe the precise paths of their oscillations and gyrations; but, nevertheless, I do admit the possibility of our conceiving, and to some extent understanding, that internal condition of matter which has been described as "molecular tension" —a condition of continuous internal statical strain, under which the constituent materials of a substance are pulling against each other, and neither of them yielding, this continuous strain resulting in extreme rigidity and brittleness; a condition which is the extremely opposite state to that of fluidity, and therefore manifesting the extreme of solidity—that is, great hardness and tenacity.

'This is generally admitted to be the condition of hardened steel, and my explanation of the cause of this condition is, that iron, although soluble, as already stated, in the fully melted Fe_4C, reasserts its original infusibility at a lower temperature, and solidifies while the carbon compound is yet in a semi-fluid or plastic condition. This must occur somewhat below the "welding-heat," or the temperature at which iron itself is plastic, or just when our theoretical alloy consists of solid molecules of iron held together by the semi-fused or pasty Fe_4C.

'As liquids in cooling contract to a greater extent than solids, the sudden cooling of this heterogeneous substance

must produce a violent molecular tension, by the resistance of the rigid iron to the greater contraction of the semi-fluid carbide, and thus we have the condition of hardened steel.

'But this is not all. Not only do liquids contract and dilate, with a given variation of temperature, to a greater extent than solids, but there is a corresponding relation between the expansion and contraction of solids themselves. Generally speaking, the more fusible solids have a higher coefficient of expansion than the less fusible. Thus, steel expands more than wrought iron, and cast iron expands still more than steel. I have no measurement of the coefficient of expansion of Fe_4C, but all analogy indicates that specular iron of this composition, being the most fusible variety of iron, should have the highest coefficient of expansion.

'Thus, according to the theory of the constitution of steel now propounded, we have a heterogeneous solid, necessarily subject to a violent molecular tension at the moment of solidification, which must go on increasing as it grows cooler. This accords with the known variations of the brittleness of steel. When we speak of the solidity or rigidity of red-hot iron, we must remember that this is by no means absolute or complete. It may be more rigid than the fusible carbide at this temperature; but although it is not sufficiently plastic to be weldable, or suddenly moulded to any shape, it is tractable enough to be forgeable, or gradually beaten, squeezed, or drawn into any shape.

'If, then, our alloy is gradually cooled from a forging-heat, it is perfectly conceivable that the more rapidly contracting carburet may *gradually* squeeze or draw—*i.e.*, forge—its more rigid associate into accommodating dimensions or more comfortable molecular positions.

'If this explanation is correct, we ought to find some evidence of the resistance to contraction in hardened steel, and yielding to contraction when the same steel is softened. The best possible evidence of this would be afforded by difference of specific gravity. The hardened steel which had resisted contraction should, bulk for bulk, be lighter than the softened steel that had yielded to condensation. What do we find?

'Let us refer to Gmelin (vol. v., page 207). He there states that the specific gravity of "hardened steel is 7·6578; of cast steel, not hardened, 7·9288."

'Dr. Percy ("Metallurgy of Iron and Steel," page 348) says:—"It has long been known that by hardening steel expands sensibly, and consequently decreases in specific gravity. Reamur seems first to have recorded the results of accurate experiments on the subject. 'M. Perrault,' he writes, 'has already observed, before us, that a steel wire, after hardening, could not pass through the same hole as before hardening. I have repeated this experiment in different ways, and I have always found an increase of volume in hardened steel; but I wished further to ascertain the extent of this increase, and whether it was sufficient to admit of being determined by measurement.'" He did so, and found that, "'in the process of hardening, steel increased $\frac{1}{48}$th of its volume.'" "'When hardened steel is re-heated to redness, and afterwards left to cool slowly, it acquires its original specific gravity, or, what is equivalent, its original volume.'"

'If my theory of the cause of the molecular tension of steel is correct, analogous tension should be exhibited by other analogous mixtures or alloys.

'An examination of the facts bearing upon this shows that such is so generally the case that we may almost

venture to state, as a physical law, that *when two metals (or substances having the leading physical properties of metals) of varying fusibilities are alloyed, the resultant alloy is harder than the mean hardness of its constituents—usually harder than either of them.*

'Thus, speculum metal, gun-metal, bell-metal, bronze, and other alloys of copper and tin, which differ considerably in their fusion-temperatures (copper 1,100 degs., tin 237 degs. C.), are all considerably harder than either of their constituents, and all admit of a certain degree of tempering. Copper and zinc also make an alloy which is harder than its constituents.

'Brass is not so hard as bell-metal and the other alloys of copper and tin, although zinc is itself harder than tin; but the melting-point of zinc is much higher (400 degs. C.) than that of tin; or, otherwise stated, the difference of fusibility of the constituents of brass is less than it is in those of bell-metal, &c.

'The two soft metals—lead and tin, which fuse at 345 degs. and 237 degs. respectively—form pewter, which is somewhat harder than either.

'In order to harden our coins, we alloy the gold, which melts at 1,250 degs., with soft copper, melting at 1,100 degs. The whole range of known metallic alloys might be brought forward in confirmation of this principle.

'Still better or closer analogies to steel are afforded by the alloys of iron with fusible compounds similar to the carbide, such as sulphides, phosphides, and silicides. The most remarkable of these is the natural alloy of iron and zinc, the Franklinite already described on page 36, which is harder than the hardest steel, and correspondingly brittle. The wide difference between the fusibility of iron and zinc accounts for this, according to my theory.

'Sulphur and iron form several definite compounds. Most of these—notably the proto-sulphide—may be alloyed with metallic iron in any proportion, and the result is much harder and more brittle than iron itself. The damage effected by very small quantities of this in wrought iron, by hardening it, and making it "red short," is well known.

'Phosphorus, in like manner, forms several definite and fusible compounds with iron, which have metallic properties. In 1781, Meyer obtained one of these from bog-iron ore, and described it as a new metal—"wassereisen, or hydrosiderum"; and two years later, Bergmann obtained the same, which he also supposed to be a new metal, and called it "siderum." This compound alloys readily with iron in all proportions, and forms a very hard, fusible substance, so hard and steely that Dr. Miller and some French chemists have maintained that steel is improved by its presence in small quantities. If mere hardness were the only quality demanded in steel, this would be the case.

'Silicon (which so nearly resembles carbon in some of its chemical relations that the late Dr. Samuel Brown, of Edinburgh, believed that he had proved carbon and silicon to be allotropic modifications of the same element) forms steely alloys or mixtures with iron so nearly resembling steel that they are actually used for some of the purposes of carbon-steel. There are certain brands of special steel at present in the market which contain as much silicon as carbon, and owe their special hardness, and, I may add, brittleness, to the silicon they contain.

'This silicon-steel appears to be an alloy of a readily fusible silicide of iron with iron, but, on account of the facility with which the silicide takes up any quantity of iron, its isolation is very difficult.

'Glass is a temperable substance—so much so that, unless it be carefully annealed after it is manufactured into its final shape, it is practically worthless. The "leer," or annealing chamber, in which the goods are gradually raised to a nearly red heat, and then as slowly cooled, is a necessary adjunct to the glass-house.

'Dr. Miller ("Elements of Chemistry," vol. ii.) says that "the different kinds of glass are not to be regarded as definite compounds, but as mixtures of various silicates in different proportions, with an excess of silica." These various silicates vary quite widely in their fusibility: those of lime and alumina are barely fusible in our furnaces while the silicates of lead, soda, and potash, so largely used in glass-making, may be fused in an open ladle over a parlour-fire. Silica itself is practically infusible in an ordinary furnace; or, quoting Miller again, "a heat as intense as that of the oxy-hydrogen blow-pipe is required for its fusion."

'Here, then, we have a substance which, although so different from steel in its appearance and other qualities, resembles it in being formed by the solution or alloying together of substances of varying fusibilities. It also resembles steel most closely in its condition of molecular tension when suddenly cooled. Glass, like steel, may not only be hardened by sudden cooling, and annealed by slow cooling, but may be tempered through a wide range of variation of softening, according to the degree to which it is re-heated.

'This, and the similar property of steel, I believe to be due to the fact that the constituents both of glass and steel do not solidify or fuse suddenly, but pass gradually, from the solid to the liquid state, through an intermediate stage of softness or semi-fluid plasticity; and this extends,

with varying degrees of softness, over a rather wide range of temperature. (It is on this account that iron is forgeable and glass is plastic at a red heat. Silica itself and the silicates have the same property.)

'In cases where the more fusible solvent fuses and solidifies suddenly—as with sulphides and phosphides of iron—the brittleness or molecular tension is not susceptible of moderation by heating to the temperature at which the fusible constituent begins to become plastic, and then slowly cooling. This incurable brittleness is, I suspect, due to the sudden solidification of the fusible medium.'

This theory, therefore, explains, not only the hardening and softening of steel by quick or slow cooling respectively, but its capability of being tempered, or varied in hardness in any intermediate degree, by re-heating to certain definite temperatures.

In the Inaugural Address to the British Association, August, 1882, by Sir C. W. Siemens, I find the following passage:—

'A recent investigation of Mr. Abel has thrown considerable light upon this question. A definite carbide of iron is formed, it appears, soluble at high temperature in iron, but separating upon cooling the steel gradually, and influencing only to a moderate degree the physical properties of the metal as a whole. In cooling rapidly there is no time for the carbide to separate from the iron, and the metal is thus rendered both hard and brittle.'

I quote this as a confirmation of my researches by a chemist and metallurgist for whom I entertain the highest respect. The confirmation is the more satisfactory as it was reached by a different route, and evidently without

any knowledge of what I had previously published. Sir Frederick Abel describes the composition of the fusible carbide as Fe_3C—*i.e.*, three equivalents of iron to one of carbon, instead of four to one, as I found it in the spiegeleisen. Further investigation is demanded, to determine which is right, or whether both are right, as may be if both compounds exist.

In 'Nature,' November 7, 1889, is a report of a Lecture delivered on September 13, 1889, by Prof. W. C. Roberts Austen, before the British Association, from which I venture to copy the following :—

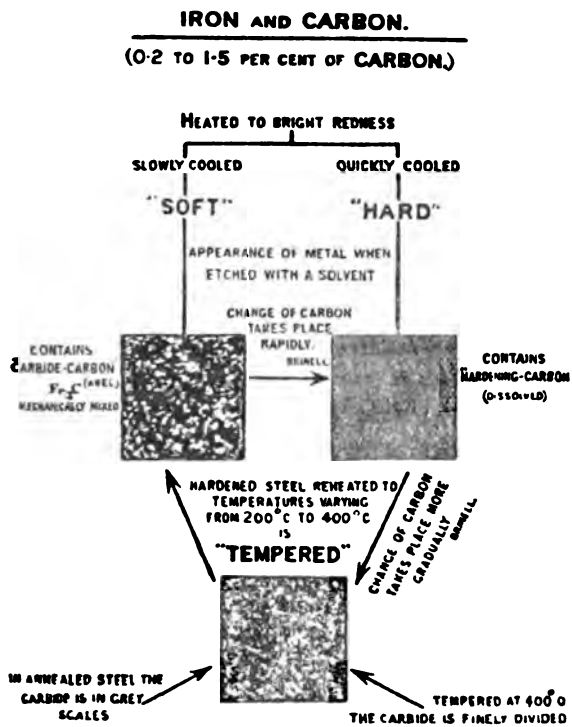
'Within the last few years Sir F. Abel has given much experimental evidence in favour of the existence in soft, cold rolled steel of a carbide (Fe_3C), which he isolated by the slow, solvent action of a chromic acid solution. His work has been generally accepted as conclusive, and has been the starting-point of much that has followed.

'It will occur to you that the microscope should reveal wide differences between the structure of various kinds of iron and steel, and I am happy to be able to give you enlarged diagrams, made from the drawings of Mr. Sorby, the eminent microscopist, which illustrated his very delicate investigations into the structure of steel.

'The point I am mainly concerned with is the existence of a substance, which Sorby called the "pearly constituent," in soft steel. This pearly constituent is closely related to the carbide of iron (Fe_3C) of Abel, and is probably a mixture of Fe_3C and pure iron. I have diagrammatically indicated its presence in the figure, which will enable me to summarise the work of many experimenters. The diagram will serve, for the purpose of illustration, to indicate the appearance when soft, hardened, and tempered steel are

respectively treated with a solvent which acts gently on the mass.'

I may add that Dr. Percy and others have arrived at


IRON AND CARBON.
(0·2 TO 1·5 PER CENT OF CARBON.)
HEATED TO BRIGHT REDNESS
SLOWLY COOLED
QUICKLY COOLED
"SOFT"
"HARD"
APPEARANCE OF METAL WHEN ETCHED WITH A SOLVENT
CHANGE OF CARBON TAKES PLACE RAPIDLY.
CONTAINS CARBIDE-CARBON
CONTAINS HARDENING-CARBON (DISSOLVED)
HARDENED STEEL REHEATED TO TEMPERATURES VARYING FROM 200°C TO 400°C IS
"TEMPERED"
CHANGE OF CARBON TAKES PLACE MORE GRADUALLY.
IN ANNEALED STEEL THE CARBIDE IS IN GREY SCALES
TEMPERED AT 400° C THE CARBIDE IS FINELY DIVIDED

the same conclusion as myself concerning the existence of a definite compound corresponding to the formula Fe_4C, but they have reached it by a different route.

Fe_3C fulfils all the conditions demanded by the propositions stated on page 327, and, being probably more fusible than Fe_4C, supports my theory still more strongly.

CHAPTER XIX

IRON *versus* STEEL FOR STRUCTURAL USES

IN 'Iron' of March 2, 1878, appeared the following:—

'THE TAY RAILWAY BRIDGE.—General Hutchinson, for the Board of Trade, practically completed his inspection of this remarkable structure on Tuesday. Six engines, each 72 tons in weight, have been employed for the test, and the greatest deflection has been only $1\frac{3}{4}$ inches. The test is more than double the greatest possible working-load which can ever come on the bridge with goods traffic, and more than three times the greatest load with passenger-trains. General Hutchinson has expressed himself as highly pleased with the results. It is expected that his report will be presented to the Board of Trade immediately, and that in the course of a very few weeks the North British Railway Company will conduct their passenger-traffic to the north by the bridge.'

My readers will, doubtless, remember the circumstances of the tragical refutation of these confident anticipations, which occurred on the night of December 28, 1879.

A gale was blowing nearly broadside to the structure, subjecting every part to a violent strain, which it successfully resisted. Presently a train of but moderate weight arrived, adding vibration to this strain, and the magnificent structure became a ruin. Such a catastrophe, and the possibility of its repetition if the same confidence as that

displayed in General Hutchinson's report is maintained, justifies me in reprinting the following paper, which I contributed to the 'Metallurgical Review' of March and June, 1878—*i.e.*, about simultaneously with the publication of that report.

If inventors were judged by their phraseology, we should be forced to conclude that those concerned in the progress of iron metallurgy are very dangerous revolutionary people. Almost every improvement of any pretensions has been heralded, either by its inventor or admirers, as an invention that will effect 'a revolution in the iron trade.' The particular revolution most prominent and popular at the present moment is that which is to be effected by the superseding of iron by steel. So far as rails and tyres are concerned, we may safely regard the revolution as actually consummated; but, at the risk of being overwhelmed by the still swelling current of metallurgical public opinion, I venture to repeat my frequently-expressed scepticism respecting the alleged or assumed superiority of steel to iron for many of the purposes to which its application is proposed, and will here state more definitely than hitherto my reasons for such scepticism.

Why is the mild steel produced by the Bessemer, the Siemens-Martin processes, &c., better suited for rails and tyres than wrought iron?

This question is easily answered, and is open to no controversy. It is, first, because the material is harder and less fibrous, and therefore resists the crushing or squeezing-out wear of rails, or the grooving wear of tyres, for a far longer time than wrought iron; and, secondly, because it is more homogeneous, and therefore wears more uniformly. We may safely conclude, that for all other

purposes where the material is subject to this kind of wear-and-tear *only*, the steel will display a similar superiority. But the revolution is proposed to extend to boiler-plates, ship-plates, girders, angle-iron, T-iron, and all other structural elements. Steel is to supersede iron in the construction of bridges, guns, armour-plates, &c. Let us take some of these in order, and separately, beginning with boiler-plates.

It is argued that steel is a better material than iron for boiler-plates because its tenacity is greater; that, as a piece of steel plate of given sectional area will resist a steady pull 50 per cent. stronger than a similar plate of wrought iron can bear, we may construct a steel boiler of $\frac{1}{4}$-inch plate that shall be as strong as an iron one of $\frac{3}{8}$, or one of $\frac{1}{2}$-inch steel plate as strong as $\frac{3}{4}$ iron, and thus gain the advantage of lightness combined with equal strength, besides diminishing the resistance to the passage of heat from the furnace to the water.

The data here stated are unquestionable. As a strip of $\frac{1}{4}$-inch plate of fair quality of mild steel will stand a pull quite equal to that which is borne by an equally wide strip of $\frac{3}{8}$ good-quality wrought-iron plate, when both of these are tried by tearing asunder with a testing machine, the above-stated conclusion appears unquestionable, seeing that the strain upon a boiler is a tensile strain, and a boiler can only burst by an actual tearing asunder of its material. In venturing to question these conclusions, I am bound to state my reasons rather fully, and will do so accordingly.

In 1868 and 1869 I made some experiments which led me to suppose that I could materially improve the quality of wrought iron by mixing oxide of manganese with the ordinary 'fettling' of the puddling-furnace, and I became, accordingly, a Patent Office victim (Specification

dated January 1, 1869, No. 4). In working this invention I tested the iron produced thereby in the usual manner, and obtained the reports which inventors usually obtain concerning the high tenacity, the extension, contraction of area, &c., of my improved iron.

Just at this time the firm of Sir John Brown & Co., of Sheffield, were competing for a Government contract for bolts for armour-plated ships, and the Government inspector, an officer of the Engineers, was at the works testing several specimens of iron offered for the purpose. He had the iron made into bolts of the required size—viz., 3 inches diameter. These were passed through two pieces of armour-plate, and secured by the head of the bolt at one end, and the nut at the other, to pieces of armour-plate as they would be in the ship's side. The enemy's cannon-ball was represented by a weight of one ton falling from a height of 30 feet, between guides, and so arranged that the force of the blow was delivered on the lower plate, to which the tail of the bolt was attached by the nut; while the plate holding the head was held firmly. The blow thus effected a suddenly-delivered tearing strain upon the bolt acting fairly in the line of its axis, and representing the strain to which a ship's bolt would be subjected when a ball had penetrated the armour, and was crashing through the backing to which the armour is bolted.

The results of this 'drop-test' were that the bolts made of certain peculiar qualities of iron stood as many as four blows before breaking. They stretched considerably at each blow, thinning to contracted waists at certain parts, the position of which was by no means constant. At the places where the maximum stretching occurred, curious symptoms of 'distress' were displayed. There were pimples and ridges on the originally smooth surface of the bolt,

evidently due to the pressure of hard, unyielding portions embedded in the more plastic material of which the bulk of the bolt was composed, showing that even the best of wrought iron is far from homogeneous. Many gave way at third, second, or first blows.

I am forced to confess that every bolt made from iron produced by my patent manganese puddled iron broke most ignominiously and carrot-like at the first blow. This was the more humiliating inasmuch as all the ordinary tests —hot and cold bends, ram's-horn test, holeing test, fractures, &c.—had given brilliant results; and the tensile breaking strain, as tested by the hydraulic machine, was unusually high, with the elongation and contraction of area quite satisfactory.

Considerable training in the endurance of disappointments enabled me to bear this; but instead of giving it up altogether, I endeavoured to discover why a sample of iron standing a direct, steady pull of above 30 tons to the square inch of sectional area should break at the first blow under the drop-test, while another sample, only bearing 22 or 23 tons of ordinary tensile strain, should hold on to the fourth blow. A good opportunity of conducting this investigation was afforded by the stock of broken bolts which remained, and were duly and systematically numbered in correspondence with the reports of a large series of drop-experiments. Having long been on very bad terms with phosphorus, which I had already proved to be guilty of much more mischief than at that time was attributed to it, I first supposed that phosphorus was the sole offender in this case, and accordingly selected a number of bolts that had stood the test exceptionally well, and others of varying degrees of inferiority. I took borings from these, and analysed for phosphorus.

The first six examined gave the following results:—

						Per cent.
A. Very good	fracture and extension,	broke at	4th	blow,	contained	0·02
B. Very bad	„	„	1st	„	„	0·15
C. Bad	„	„	1st	„	„	0·07
D. Bad	„	„	2nd	„	„	0·13
E. Good	„	„	4th	„	„	0·07
F. Good	„	„	4th	„	„	0·05

Here was an indication that phosphorus had something to do with the mischief. It might be found guilty on the evidence of A and B, but that of C and E were suggestive of something else. I made several other analyses, with similar results. Every bolt containing an excessive percentage of phosphorus stood the test badly; but, on the other hand, there were rejected bolts containing very little phosphorus—no more than other good bolts, as in the cases of C and E above.

On further examination of the recorded experiments, I found that in almost all cases the samples of iron which stood an excessive breaking strain when tested by the gradually-increasing pull of the hydraulic machine, failed when subjected to the drop-test, just as my manganese iron did.

For example, a steely iron containing 0·18 per cent. of combined carbon, which showed a breaking strain of 34·18 tons per square inch, with an elongation of 12 per cent., broke at the first blow of the drop-test, with scarcely any elongation. The iron finally selected and used for making bolts showed a breaking strain of 22 to 24 tons per square inch, and usually broke at the fourth blow, with good elongation.

This, of course, pointed to carbon as an accomplice with phosphorus.

I had already discovered, in the course of my experi-

ments with the manganese fettling, that the first ball drawn from the puddling-furnace differed materially in some respects from the second and third. The iron made from the first ball bore a stronger pull in the hydraulic testing machine than that from the second, and the second more than the third. The first ball bore most of the *hot* tests (punching hot, bending, &c.) better than the third; and, generally, the third bore the *cold* bending tests better than the first. Analysis showed that they all contained an appreciable amount of carbon, and that this was always greatest in the first ball, and progressively less in the later balls. To test this more severely, I had some heats made into four or five balls, instead of the customary three, and the results were in strict correspondence with the above.

The reason of this is obvious enough. The ball of spongy, uncompressed iron, as it stands in the puddling-furnace, waiting its turn at the hammer, is undergoing oxidisation; but the oxygen first attacks the carbon, which continues to protect the metal so long as it remains in sufficient quantity: and thus the only difference between these different balls from the same heat is their different proportions of carbon.

This supplied me with the means of making an *experimentum crucis*, by having two bolts made—one from the first ball, the other from the third ball of the same heat of 'best best' iron, puddled in the ordinary way. The first ball was hurried off to the hammer as sharply as possible, and the third was delayed rather more than usual.

The first contained nearly $\frac{2}{10}$ per cent. of carbon, the third a barely visible trace, too small to be determined quantitatively by the ordinary methods of analysis. The bolt made from the first ball broke at the first

blow that from the third, at the fourth blow. They were not officially tested, but I have no doubt that, had they been, the first would have been rejected, and the second accepted, though both were made from the same heat. (I need scarcely add that, in practice, the three balls are usually welded and rolled together, and thus a bar of mean composition is obtained.)

The above details are given because they have a direct and, I think, important bearing upon the question now occupying so much attention among the metallurgists of all nations. In the case of these bolts, the steely attributes were directly detrimental. Increased tenacity, as measured by the application of a gradually-increasing strain, was accompanied by increased weakness in relation to a sudden shock. The case is an extreme one, undoubtedly, and the test excessively severe; but admitting this as regards *degree*, does it not represent the *kind* of strain to which boilers, girders, ship-plates, bridges, and all structural applications of iron or steel, are more or less subject.

Let us take a boiler first. While the heat is being gradually applied, the expansive force of the steam gradually developed, and the boiler firmly at rest, the plates are submitting to a strain fairly represented by the hydraulic, or screw-testing machine; but if, when the metal is thus strained, the boiler is submitted to any kind of shock, the conditions are entirely changed: a vibration traverses its structure; waves of compression and extension suddenly add to the tearing strain of the expanding steam in one place, and diminish it in another.

The boilers of all kinds of marine engines and of locomotives are subject to violent vibratory shocks. Suppose we have two boilers—one of steel, and the other of soft, malleable iron—and both have been tested by

hydraulic pressure to the same extent. Which would be the most likely to give way under practical conditions, and subjected to ordinary and extraordinary shocks while worked nearly up to their tested pressure?

If compelled to sit on the safety-valve of one or the other, I should choose the soft iron.

It is well known that some of the worst cases of boiler explosions have occurred very unaccountably, as though some sudden generation of expansive force had occurred. The spheroidal state of water, its decomposition by the overheated plate, followed by explosion of the gases, and other theories, have been invented to account for these. The fact of sudden shock of some kind can scarcely be disputed, and steel plates, if I am right, would, in spite of greater tenacity to steady strain, be the weakest when subjected to such sudden violence.

Girders, and the supporting element of bridges, are so especially liable to vibratory shocks, that mere tenacity under a gradually-applied and steady strain is of little or no value in reference to them, unless it indicates a corresponding resistance to the particular shocks which most endanger their stability. The experiments above described, so far as they go, indicate very ominously that such is so far from being the case that a high degree of tenacity actually indicates practical weakness. I say 'so far as they go,' being fully conscious of the inadequacy of so small a series of experiments to establish so important a conclusion, and the great desirability of further and searching investigation of the subject, especially in reference to different kinds of shock.

A rigorous course of researches should be instituted, in order to determine with quantitative accuracy what I may term the neutral, or turning, point of tenacity as

ordinarily tested. Assuming that I am right in claiming for good soft wrought iron a higher degree of practical strength or resistance to the shocks and strains to which structures are subject than steel, it is very desirable to determine the tenacity of good iron, as compared with the higher tenacity of steel and lower tenacity of bad iron, in the condemnation of which we all agree.

In advocating these further investigations, I am not forgetting what is actually and commonly done in the application of the drop-test to steel rails, &c., and am aware that much has been done at our British arsenals, though not acquainted with the details of all these experiments. Their teachings are suggestively indicated by the fact that, in its specifications for 'angle, bulb, or bar steel,' the British Government now demands, as a fundamental requirement, that 'the whole of the steel shall stand a tensile strain of 26 tons to the square inch, and *not exceed* 30 *tons to the square inch.*'

This indicates a considerable revolution in authoritative opinion, for, in February, 1869, when I ventured to state, in the course of a controversy in the 'Chemical News,' that excessively high tenacity, as indicated by a gradually-applied strain, is an indication of practical weakness rather than practical strength, I stood in opposition to high authorities, who, in reporting on the merits of samples of steel containing much phosphorus, commended them as excellent for structural purposes simply *because* they bore a tensile strain of above double that which is now demanded. (See Chapter XII. for details.)

The results of the above-described bolt experiments (which were reported to the Admiralty), and others with which I am not acquainted, have evidently led to the wise restrictions of our Government specifications. Inventors

who are seeking to prove the superiority of their iron or steel by advertising its high tenacity, should not lose sight of the fact that high tenacity in wrought iron is usually an indication of unremoved carbon.

I need scarcely add, that all the above remarks apply to the question of iron *versus* steel in the construction of ships. No novel experiments are needed to show that, if a ship is bumped against a rock, a soft iron plate, capable of considerable indentation, is incomparably safer than one of brittle steel.

The complex and difficult process of building huge armour-plates of 20 to 30 tons weight by welding together four or five hundred or more puddled balls, naturally suggests the substitution of a material which, besides being harder, and apparently stronger, may be manipulated so much more readily. With an easily-attainable modification of existing appliances, the material for such a plate may be cast in a single ingot of steel, and rolled at once into shape. Many attempts have, accordingly, been made to substitute steel armour-plates for iron. Such plates have been made, and, so far as hardness and tenacity—tested by steady strain—are concerned, they have been proved to be far superior to the armour-plates that now clothe our great ironclads.

When subjected to a test resembling that applied to the bolts—*i.e.*, when exposed to the crushing blow effected by the point-blank battering of heavy ordnance—they have displayed great powers of resistance to the direct penetration of the shot, excelling the iron plates very decidedly in this respect, but, at the same time, revealing a far more dangerous weakness—that of cracking, splitting, and even breaking up into a wreck of fragments. Some experiments made on the 'Nettle' target-ship, on the

18th December last (1877), are so instructive that I will quote the results:—

Messrs. Cammel, of Sheffield, sent three plates. No. 1, a solid plate of very mild steel, the carbon kept as low as practicable, and treated in its manufacture with the special object of toughening, or reducing the liability to crack or 'star.' Its dimensions were 9 feet 9 inches by 7 feet 9 inches, and 9 inches thick; it weighed 12 tons 3 cwt.

No. 2 was a compound plate; total thickness, 9 inches; 5 inches of hard steel in front, welded, by a patented process, to a backing of 4 inches of soft iron. It was supposed that the hardness of the steel front would resist the first impact of the shot, and probably break it up; while the iron backing would arrest the cracks, or starring of the steel, and prevent their extension throughout the whole thickness of the armour, the vessel, consequently, remaining water-tight, and the plates still standing to receive other shots. This plate measured 9 feet 9 inches by 7 feet 1½ inches, and weighed 11 tons 4 cwt.

No. 3 was a sandwich-plate, made up of a layer of steel between two of iron: the middle steel layer, 6¾ inches thick; the front iron layer, ¾ inch, and the back iron layer, 1¾ inches. It measured 8 feet by 5 feet 11 inches, and weighed about 7 tons 16 cwt.

Competing with these was a curious complication sent by Sir Joseph Whitworth—a plate made up bodily of Whitworth's fluid pressed steel of low carbon. This plate was then drilled through, at certain uniform distances, with holes 4¾ inches in diameter, and into each of these holes a hardened steel plug was screwed. Like the others, its thickness was 9 inches, its other dimensions, 6 feet 8½ inches by 4 feet 11½ inches. These four plates, duly attached to the shield representing a ship's side, were

attacked by Palliser shots weighing about 250 lbs., fired from a 12-ton Woolwich gun, charged with 50 lbs. of pebble powder.

The Whitworth plate came to grief very speedily. I am not at all surprised at this, but am very much surprised that such a thing should ever have been constructed. In excuse for its failure, the 'Times' newspaper pleads that it had not been 'oil-hardened,' as intended.

I am quite unable to understand how oil-hardening or oil-toughening could improve such a heterogeneous mass. If the high carbon steel pins were fully hardened before insertion, a milder hardening by oil would diminish their size without equally diminishing that of the mild steel body of the plate. If soft when screwed in, the oil-hardening would expand them considerably. In the first case, the resisting power of the plate would probably be diminished by the aid of the series of skilfully-initiated fractures, as a vibratory jar or sharply-localised shock would occur when the vibration caused by the shot reached the lightly-touching surfaces between the plate and pin. In the second case, the expansion of the pins would subject the whole plate to a strain or tension at every hole, the force of which would come in aid of just the sort of rupture to be avoided—viz., a cracking across from hole to hole, and consequent detachment of the intervening piece.

The composite plates, Nos. 2 and 3, both split up badly, 'their complete disintegration being effected by the third shot.' The only one of the four that stood the ordeal at all satisfactorily was No. 1—the homogeneous soft steel plate. This showed only a few indentations and hair-cracks, with some bending inward. Like all the steel plates that have been hitherto tested, it resisted penetra-

tion better than wrought iron, but was weak in reference to cracking.

A shot may penetrate a good soft iron plate, leaving a hole not quite as large as the shot. If there is no cracking, the mischief ends there—the pierced plate still stands as at first for other shots; but a plate fractured even by hair-cracks grows worse at every succeeding shot, and finally breaks to pieces.

The practical conclusion to which all the above-stated facts and reflections point is, I think, that for all purposes where resistance to vibratory shocks or suddenly-applied strains of any kind is demanded, the old-fashioned wrought iron is more reliable than steel of any kind that is at present obtainable. I do not, however, maintain that we should be satisfied with this conclusion, but, on the contrary, regard it as indicating the direction of future effort, which should be devoted to the softening and toughening of these new steels, in order to combine, as far as possible, some of their valuable properties with those of wrought iron.

If the only difference between mild steel and soft wrought iron were that already discussed, and which is usually so prominently put forward in favour of steel, I should have no hesitation in carrying my heresy so far as to maintain the absolute superiority of iron to steel for all structural purposes; but we must not forget that carbon, even in very small proportions, confers on iron another property besides those of increased hardness, increased resistance to steady tensile strain, and proportionally increased brittleness. It renders it practicably fusible; and by availing ourselves of this fusibility, we may obtain the very great advantage of a homogeneous metal. To appreciate the magnitude of this advantage, we must remember

the mechanical axiom that 'nothing is stronger than its weakest part.'

Wrought iron is an agglomeration of the unfused granules that separated from the cinder when the metal 'came to nature' in the puddling-furnace. These are gathered into a spongy ball by the puddler, and welded together more or less completely under the hammer or squeezer. They are then united to another similarly-constituted ball, and further welded in the course of rolling, &c. The fact that a plate thus made is so much stronger when tested by a longitudinal strain than by one applied crosswise to the direction of rolling, strikingly indicates its want of homogeneity.

It is obvious that any kind of steel, whether hard or mild, which has been fully fused, and well agitated while in a state of fusion, does not share this defect, provided that every separate element of the structure, or every plate, is made from a single ingot.

Just at the commencement of my Sheffield experience the practical homogeneity of Bessemer steel was a subject of considerable controversy. The question at issue was this: After the 'blow' is completed, the converter contains fused iron nearly free from carbon (the oft-repeated statement that *all* the carbon is burnt out is a mistake); to this, which we may call soft iron, the intensely hard and brittle, highly carburetted spiegeleisen is added. In the ordinary course of manufacture, as then and there practised, the mixture was immediately poured into a large pot or 'laddle,' and from this into the ingot-moulds, by simply lifting a plug from the bottom of the laddle while standing over the ingot. No special means of agitation were adopted, and it was maintained by some of the Government officials and other customers that this was insufficient

to ensure a complete admixture of the decarburetted pig with the spiegeleisen. Like most others who had not gone fully into the subject, I at first shared this opinion, while the manager of the Bessemer department, the late George Brown—to whom Mr. Bessemer and all the world are so much indebted for his valuable contribution to the difficult work of rendering the Bessemer process practically efficient—stoutly maintained that the admixture was so completely effected by what occurred automatically in the converter that no kind of supplementary stirring could improve it.

He took some pains to convert me to his view, and succeeded. He had erected a small platform from which a view was obtainable of the interior of the converter during the pouring of the spiegel. At first nothing could be seen but a white glare of painful brilliancy, but by gazing steadily the surface of the melted metal became distinguishable. It was then seen to be in a state of furious commotion, similar in character to the 'boiling' in the puddling furnace, but far more vigorous. After carefully watching this during a few operations, it was impossible to resist the conviction that complete admixture must be effectually secured by this action.

George Brown supposed that this was due to oxygen left in the melted metal after the blow. Subsequent investigations of my own proved that he was right so far as the existence of oxygen is concerned, but it was not there, as he and others supposed, in the form of occluded gas, but as minute black grains or powder of magnetic oxide. This I have demonstrated both by chemical and microscopical examination. When the spiegel is added the carbon reduces this oxide by combining with its oxygen, and the effervescence is due to the escape of

carbonic oxide, which produces the vast volume of beautiful blue flame that rises from the mouth of the converter during the pouring in of the spiegeleisen.

To satisfy some sceptical customers, certain casts of very mild steel were subjected to further agitation by turning back the converter after the addition of the spiegel, and blowing through it during a few seconds. I agree with George Brown in regarding this as quite unnecessary, and even believe that it is attended with some risk of over-blowing, and thereby introducing an admixture of some quantity of the oxide particles above described.

We may safely assume that Bessemer steel made with ordinary care is practically homogeneous throughout any given ingot. I say 'practically,' because absolute homogeneity is impossible, seeing that superficial oxidation always occurs when iron or steel is heated in the air. In the case of steel the carbon is attacked, and thus its proportion is locally diminished. It would be mere hair-splitting to make any practical quibble upon this ground. The same may be affirmed of the mild cast steel now made by the Siemens-Martin and other similar processes.

But is it quite certain that such homogeneity is an unqualified advantage in all cases?

At the risk of anathema I answer 'No,' and even venture to affirm my belief that a certain amount of structural or molecular irregularity, such as that of good wrought iron, is, for some uses, decidedly advantageous, as it must check or deaden the transmission of destructive vibrations.

I further venture to suggest that such degree of irregularity combined with softness may be conferred on steel by elaborate and scientific annealing.

There are many methods of annealing steel, and two distinct principles involved in these. The first principle

is that of softening and toughening simply by slow cooling. This I may call ordinary annealing. The second principle, which is less commonly practised and still less commonly understood, is quite different. It is an inversion of the cementing process—a partial or total reconversion of steel to iron.

The first principle is so well understood that I need say but little concerning it, except to narrate some curious experiments that I commenced when in Sheffield, but have not satisfactorily completed.

They were made at the suggestion of the late Mr. William Bragge, then the managing director of Sir John Brown's works. He had learned that the steel wire strings of pianofortes are annealed by what appears a very anomalous process, viz., by making the wire red-hot and then plunging it into *boiling water*. Ordinary experience would suggest that this must harden the steel in some degree, but I tried it upon many samples of steel, on mild Bessemer steel, on shear steel of different qualities, and on the hardest old-fashioned Sheffield 'pot steel,' and found that in every case, when the operation was properly performed, the steel was remarkably toughened. I compared samples cut from the same bar, one heated and slowly cooled by burying in ashes under a furnace grate, and the other by immersion in boiling water, and found, that when subjected to bending tests, those which had been cooled in the boiling water would bear a more severe degree of flexure without cracking than the pieces which had been much more slowly cooled in ashes. They were not so soft as tested by the touch of the file, but unquestionably tougher, and more reliable when subjected, while cold, to violent bending blows of a hammer.

Other engagements carried me away from the further

prosecution of these experiments, and thus I am unable to say how the power of resisting ordinary tensile strains or drop tests was affected by this method of cooling, and can only record my general impression, derived from the peculiar character of the bend (the remarkable contraction at their convexities and expansion at their concavities, &c.), that it was more effectual than any device of 'oil toughening' I have had opportunities of testing.

Certain precautions are necessary. In the first place, the water should be quite at the boiling point, and the steel at a bright red heat; and, secondly, the steel should be fairly surrounded by the water. These conditions being fulfilled, the steel remains red-hot under the water for some time. It is evidently surrounded by a film of vapour, and is not in actual contact with the water, which assumes the so-called 'spheroidal state,' and remains in this condition until the metal has cooled considerably. I suspect that the toughening is due to the uniformity of cooling thus effected.

I commend this method of annealing or toughening to the attention of manufacturers engaged in the production of all kinds of steel that is to be used for purposes where tenacity rather than hardness is demanded. It would be a very interesting experiment to make a large armour-plate of Bessemer or other mild homogeneous steel, cut it in half, then treat one half as usual and the other in this manner, and submit them both to battering tests, such as are applied at Shoeburyness.

It is, however, to the second method of annealing that I look for the perfection of the steel; or, rather, the structural metal of the future.

I have made a large number of experiments upon the effect of heating steel and exposing it while hot to the

atmosphere or other oxidising agents. By taking filings from the surface, and borings very near the surface, and at different depths below the surface, and analysing them, I have found that the carbon of the steel is oxidised at the surface more or less completely according to the temperature and degree of exposure, and also that this oxidation *penetrates below the surface;* that a piece of hard steel may thus be converted into soft iron, just as a piece of soft iron may be converted into hard steel by cementation, and that the action is strictly analogous, but diametrically inverted.

The general results of these experiments justify the inference that both actions, when conducted under correspondingly favourable circumstances, proceed at about the same rate—that is to say, a given proportion, say 0·5 per cent. of carbon, may be taken out of a given-sized bar of steel in about the same time as it may be combined with a similar bar of iron by the process of cementation.

The results are otherwise analogous. The steel produced by cementation, as is well known, is not homogeneous, the outside of each bar being harder than the interior, owing to the greater proportion of carbon on the surface and its gradual diminution inward. In like manner, the outside of each bar of steel submitted to oxidation is softer than the interior, owing to the greater degree of oxidation on the surface and its gradual diminution inward.

There are several methods of effecting this oxidation, the simplest, of course, being that of exposure to the atmosphere. This, however, is not the best. Immersion in oxide of iron or oxide of manganese, or a mixture of both, is preferable. The steel should rest on a bed of oxide and be covered with the same, and in this condition be heated

continuously in a cementing or annealing furnace. Bars may be packed in alternate layers with oxide, just as the bars of iron are packed with 'cement powder' in the old-fashioned manufacture of steel by cementation.

To illustrate my notion of the advantage of this, let us suppose that I am a manufacturer of armour-plates, and that I am invited to a competition at Shoeburyness. I should make my model armour-plate as follows:—

First, cast a single ingot of mild Bessemer steel of the weight demanded for the plate in the rough; then forge and roll in the usual manner to the thickness required for the rough plate, and cut it to its intended length and width without planing down its surface. Having proceeded so far, I should bed the plate in a mixture of oxide of iron and oxide of manganese, finely powdered, and also in the same furnace and in like manner bed some scrap-ends cut from the rough plate. The whole should then be heated to a full cherry-red, and be kept thus for about a fortnight. I should then take out one of the scrap-ends and make borings at different depths on its surface, and determine the carbon of these by Eggertz's method. If I found that the surface and the substance of the metal, down to about an inch in depth, were so far deprived of their carbon as to give no appreciable colour to the solution in nitric acid, and that the middle of the plate contained about one-quarter per cent. of carbon, I should regard the softening process as completed, and the plate ready for planing and finishing in the usual manner. If it retained more carbon than this, the softening would be carried further by continuing the heat for some time longer.

Considerable experience would be necessary to determine beforehand the approximate time required for such an extent of oxidation. It might be much longer than my

supposititious fortnight. By this means a plate would be obtained composed of a mild steel core, enveloped in a soft iron integument. It would, therefore, cease to be homogeneous, but the variations of its composition would be regular, graduating steadily from the softest of iron outside to mild steel within, with no sudden break of composition corresponding to that of 'sandwich plates.'

My expectations of the stability of such a plate are founded on the fact that the cracking of a steel plate or bar when subjected to a vibratory shock must of necessity start from the surface. We see this when the fracture is partial, as in bending, or when hair cracks are made in armour-plates. The soft iron integument would resist this, while the steel core would give hardness and increased tenacity.

The same principles and method are applicable to boiler plates, ordinary ship plates, girders, T-iron, angle-iron, &c. The case I have selected for typical illustration presents the greatest difficulty, on account of its size and thickness.

Thinner plates and other lighter articles may easily be treated thus without the risk to which a thick armour-plate would be exposed—viz., that of oxidising the iron on the surface before the oxidation of the carbon had penetrated deep enough. Skilful management would be necessary in order to avoid this, but I have no doubt at all that with such management it may be done.

I offer the above as crude suggestions for the consideration of those who are practically interested in the subject, believing that if the principles are worked out they may be of considerable practical value.

For some purposes the toughening by boiling water would probably be preferable to the decarburetting of the

surface. The piano-strings present a case in point. These demand great tenacity in order that they may bear the pull required to bring them up to pitch. They are subject to vibratory shocks, it is true, but these shocks are of an orderly and regular character, the string being arranged and stretched to ensure this regularity. The fair undulations of a thin yielding string or wire are very different from the sharp, short, irregular vibrations of a thick bar or other mass of metal when struck or shaken at random.

It may be objected that by taking away the carbon the surface of the metal would be left porous. I have not examined the surfaces with sufficient minuteness to deny this, but certainly have seen no evidence of such porosity on any samples subjected to my experiments.

But I can offer better testimony than this—viz., that afforded by the steel engravers. They anneal their plates until the surface becomes soft iron. If the surface were rendered sensibly porous thereby, it would be spoilt for their purpose. From the analogies of similar actions it is more probable that contraction would occur than that the hot metal should become porous. The effect of such decarburetting on tenacity is a point demanding further investigation, as, in fact, does the whole subject.

During the twelve years that have elapsed since the above was written considerable progress has been made in the direction of producing very mild steel, or 'homogeneous iron,' by carefully working the Siemens-Martin process. I have seen and examined samples of wonderful softness and toughness, some of them superior to wrought iron in the special attributes that I have above claimed as constituting the superiority of wrought iron for the purposes named; but as 'nothing is stronger than its weakest part,' there remains the danger of some portion of a structure being made from an over-hard ingot, the hardness of

which has escaped detection. This risk would be greatly minimised, might be quite eliminated, if every portion were carefully annealed in the manner I have suggested. The practicability of such annealing is shown in the 'malleable iron castings,' which are very well known but not so well understood. The mystery of their production is unveiled by the preceding.

Suppose we take some pig iron containing very little silicon, or, what is chemically equivalent, some ordinary iron that has been refined, which fining, as explained on page 127, removes most of the silicon; make small castings from this, and then subject these castings to slow heating and cooling. The result will be a combustion of more or less of the carbon they contain, and the consequent production of impure malleable iron. The less sulphur and phosphorus in the original pig the nearer will these annealed castings approach to the composition of wrought iron. If I am not altogether mistaken, the success of this production of malleable castings primarily depends on the selection of the foundry iron.

As the importance of distinguishing between tensile strain and vibratory shock is of such serious, such vital importance, and as it is still so imperfectly understood in reference to the use of iron *versus* steel, I cannot refrain, even at the risk of over-reiteration, from adding further explanation.

Steel is more elastic than iron, and this elasticity increases within certain limits with the quantity of carbon it contains. It is, therefore, subject to greater vibration than soft iron, or, in other words, waves of compression and extension are more freely and completely transmitted through its substance. This difference is distinguishable when a number of iron and steel rails are being loaded or unloaded together. The clang of the steel rails is more

musical than that of the iron rails, the 'ring' of the metal is better. Now this 'ring' is simply due to continued vibration, and such vibration is an alternate compression and extension of its substance, or, as some would say, an approximation and separation of its molecules.

This may be shown by the following simple experiment. Take a straight bar of steel, and clamp it firmly by the middle to a bench or table. Place a marble or other movable body on the table, and firmly touching one end of the bar. Now strike the other end smartly, but not heavily, with a hammer. That part which receives the blow of the hammer is compressed for a moment; being elastic, it reacts or expands again; in doing so it pushes forward and compresses that part of the steel next in front of it, this second compression reacts again on another portion farther on, and thus the wave of compression is transmitted to the other end of the steel, and shows its force by reacting against the marble and driving it away, although the piece of steel as a whole is not driven forward at all. The marble starts away from the one end of the bar almost at the same moment as the blow is struck on the other, showing the rapidity of transmission and consequent suddenness of the strain.

If the vibration is produced by a sudden bending shock, the transverse extension and condensation strain is still more violent, but the most disruptive effect of all results from the collision of two or more different sets of such undulations meeting together from different directions. An instructive and rather striking illustration of that is occasionally afforded when a sound steel rail is broken by merely falling obliquely on its end from a waggon. In such cases, it appears that the rail has received two smart, though not heavy blows: one at the end striking a stone

or other hard substance on the ground, the other by collision with the other rails or the ironwork of the waggon. Vibrations thus start from each end, and the fracture occurs where they meet.

The effectiveness of this kind of shock may be studied by watching the beating of water waves or ripple against a sea-wall, or other perpendicular embankment. The reflected waves on their return meet those advancing, and where they coincide do not merely throw up a wave of theoretical height, viz., equal to the sum of the two waves, but dash upward a certain quantity of water to a far greater height than this, with a spurting suddenness that indicates a very powerful collision and compression of a limited portion of the water.

To prevent a possible misunderstanding, I will further explain what I mean by the elasticity of steel. A substance may be highly elastic, perfectly elastic, although its range of compressibility or elongation be very small. This is the case with ivory. A billiard ball illustrates this. It rebounds with mathematical accuracy (as indicated by the equality of the angle of reflection to that of incidence), or so close an approximation to it that the deviation is not measurable. Every time it strikes another ball it is indented at the point of impact, but recovers so completely that a hundred thousand blows fail to effect any visible deformation. Thus its elasticity or 'energy of restitution,' i.e. its power of regaining its form and dimensions, is greater than that of india-rubber, which if similarly treated would become deformed or acquire 'a permanent set.' But the *range* of elasticity of india-rubber is very great, while that of ivory is very small. This range being plainly visible, gives rise to the common idea that the india-rubber is the more elastic of the two.

CHAPTER XX

THE STABILITY OF IRON

A GREAT deal has been written and spoken concerning the molecular changes produced in iron by vibration, and many instances are cited of iron that has shown a crystalline fracture after long exposure to vibratory disturbance. But those who theorise upon the so-called molecular changes due to such action, base all their conclusions on a few exceptional facts, and apparently forget the multitude of other facts which contradict their theory. Ordinary experience shows that good iron remains fibrous throughout its substance after years, and even centuries, of considerable vibratory wear and tear. This broad general fact throws much suspicion on the isolated cases of crystalline structure attributed to vibration.

If vibration is a true cause of crystalline structure, then crystalline structure should follow as an invariable consequence of vibration. This is certainly not the case, and therefore where the crystalline structure has been occasionally found we should look for another cause. This, I think, is not difficult to find, viz., in the original bad iron. It is no reply to this to point to the fact that one part of the piece of iron in question was fibrous, and the other portion, that is supposed to have suffered, or really may have suffered more vibration, was crystalline, because, as every practical ironworker knows, we may find fibrous and crystalline

iron, not merely in different fractures of the same bar, but even in different portions of the same fracture. Inferior, ill-worked iron is especially liable to such irregularities of structure.

The theory that localised crystalline structure is produced by vibratory action may sometimes be very convenient for contractors, but I doubt whether it has any reliable foundation in fact.

The above remarks must not be understood as implying that vibratory shocks may not weaken iron. There are many incontestable facts which prove that a vibratory shock, if sufficiently violent, certainly does effect such weakening. I need only refer again to the trials of armour bolts by the falling test, already described. Here we had a definite force applied as a sudden shock, a weight of one ton falling thirty feet. The first blow is resisted by the best iron, the second blow also, likewise the third; but, on applying the same amount of force in the same manner a fourth time, the iron yields, showing that the previous shocks had weakened it, and rendered it unable to resist a blow that it was previously able to bear.

But was this weakening due to the development of crystalline structure?

Certainly not. The alteration of structure indicated by the best iron was rather in the opposite direction. The 'distress' exhibited after the first blow, and more and more obviously displayed after the second and third, presented the appearance of a dragging or stretching out of the fibres, a sort of exaggeration of the normal fibrous structure of the iron. In those parts where the extension and consequent reduction of diameter was the greatest, the fibrous structure of the iron was to a certain extent visible on the skin of the metal, and the final fracture of

the best samples had a brush-like character, due to this dragging out or exaggeration of fibre. These appearances are also observable when the best iron is broken by a gradually applied tensile strain, and may be studied in some beautiful samples of fracture that are preserved by Mr. Fairbairn.

It is true that in these cases the strain has been exerted only in one direction, and doubtless the effect would have been different had its direction varied; but what would be the extent of this difference?

Merely, I suspect, to neutralise the dragging out or exaggeration of fibre, but not to substitute for this another and very different action—viz., the development of crystalline structure. I do not at all question the conclusion that a long continuance of small vibratory shocks may possibly weaken iron or steel by gradually effecting a similar 'distress' to that so plainly exhibited and suddenly produced by the violent shock of the falling test, but do maintain that we have no sufficient or even approximately sufficient evidence in support of the theory that vibration can convert fibrous into what is called crystalline iron.

A further and full experimental investigation of this subject is imperatively demanded, and may readily be made. Cut a good plate or bar into at least twenty equal pieces; shuffle them well, then take ten and ten. Let the first ten be laid aside in a quiet place, and the other be exposed to continuous and sharp vibration for a year or two. Attaching them to a tilt-hammer regularly used for shingling the faggots of blistered steel, and making about 300 strokes per minute, would do very well for this purpose. Then let each two be tested for tenacity, and their average tenacity compared.

I say at least twenty, because all wrought iron is more

or less variable in cohesive power at different parts of the same plate or bar, and thus the more numerous the trials and broader the average, the more reliable the result; and 'shuffled,' because if one set were all middle pieces, and the other all side or end pieces of the plate or bar, the trial would be delusive.

There is another and very curious question connected with this subject that also demands similar investigation, its practical and philosophical interest being considerable. It is whether iron and other inanimate substances are susceptible of becoming weakened by 'fatigue,' and of recovering in some measure by repose. Many may smile at the bare suggestion of such a question, but it is not so ridiculous as it may appear. Intelligent workmen, whose daily experience constitutes the broadest of experimental data, assert that the tilt hammers of steel works, which work with the greatest rapidity, give way near the axis unless they are allowed intervals of rest. I have never had an opportunity of verifying this or any other similar cases, but, nevertheless, see no good reason for discrediting it, nor any great difficulty in understanding how it may occur.

When iron, steel, or any other elastic substance is subjected to a gradually increasing strain, the first indication of distress is an elastic extension, that is, an extension which is partly or wholly recovered when the straining force is removed. Now let us suppose that the total breaking force in any such case is $=a+b$, where a is the amount of force sufficient to produce an elongation recoverable by elasticity; it is evident that when the substance is in this condition, the strain by which it may be broken is a smaller force than when in its normal state; it is b instead of $a+b$, or otherwise it is weaker in this condition

than when at rest. If, then, the recovery from the state of elastic strain is not instantaneous, but demands some time, a period of rest equal to that time is demanded, in order that the strained material may recover from its fatigue.

The question is thus reduced to whether complete recovery by elasticity is instantaneous or occupies some time, and how great is that time? Also, whether this period of recovery varies with different substances? There can, I think, be little doubt that an appreciable time is demanded, that the length of that time varies considerably, and is intimately connected with that internal friction which has been described as molecular viscosity.

The effect of temperature on the stability of iron and steel has been recently treated rather fully in 'Iron.' (This was written in 1874.) Putting all the reliable experiments and other data together, I think I may venture to generalise to the extent of saying that *lowering of the temperature of iron or steel affects its powers of mechanical resistance in nearly the same manner as the addition of carbon, silicon, or phosphorus, the resemblance being nearest to the action of phosphorus.*

If this is correct, then the effect of intense cold on iron or steel will be to increase its brittleness when subject to a vibratory shock, while it increases its tenacity as tested by a gradually applied and steadily increasing strain, and the effect of raising its temperature is the converse of this—i.e., a given sample of iron will be less liable to fracture by mere vibration when hot than when cold, and weaker when tested by a steady pull.

I may also venture to express my belief that the presence of sulphur, within certain limits, tends to mask this difference, but not to fully counteract it, while phos-

phorus, silicon, and carbon materially exaggerate it. Or, in other words, sulphur diminishes the differences due to a given variation of temperature, while phosphorus, silicon, and carbon increase it.

Those who have studied this subject and are disposed to prosecute it further, will, I think, find in the above inductions an explanation and reconciliation of most of the apparent contradictions which recorded experiments present.

Next in importance to the structural sources of weakness to which iron and steel are subject, that of surface deterioration naturally presents itself. The fact that forty tons of oxide were recently scraped away from the Menai Bridge, in the course of cleaning, indicates the magnitude of this action. All forms of matter are subject more or less to atmospheric influences, but there are some peculiarities in the mode of atmospheric action upon iron which place it almost alone, and these have scarcely received the attention they deserve.

That iron is subject to oxidation by the combined action of air and moisture is one of the most familiar of truisms, but that the manner of oxidation of iron is essentially different from the manner of oxidation of lead, or copper, or zinc, or tin, or most other metals, is by no means generally understood. If this difference were one of a purely philosophical character and only interesting to theoretical chemists, I need not here discuss it further, but as it is essentially practical and must form the basis of any successful effort to prevent or diminish the gradual decay of iron, it demands the careful attention of engineers and all who are practically concerned in the erection or maintenance of iron structures.

Let us first inquire what occurs when a surface of zinc,

lead, or copper is exposed to ordinary atmospheric action. In the case of zinc, oxidation rapidly takes place, for zinc is electro-positive to iron, and its direct affinity for oxygen under ordinary circumstances, is considerably stronger than that of iron for oxygen. Neverthless, it stands exposure far better than iron, so much better that we protect iron from atmospheric action by 'galvanising' or coating it with zinc.

A little examination will show how the zinc is preserved. If a surface of smooth bright metallic zinc is exposed to the air it rapidly tarnishes. A careful examination of this tarnish shows that it is a smooth continuous surface, forming, in fact, a film of most compact and solid varnish, which effectually protects the metal below from further atmospheric action. It does this partly by virtue of the unbroken character of the film, and further, and most materially, because this oxide is the only one of zinc that can be thus formed, and it is not soluble, or otherwise removable by ordinary atmospheric agencies. Thus, the oxygen of the air performs the contradictory function of preserving the zinc against its own ravages.

If, however, a zinc roof is exposed to an atmosphere carrying the fumes of hydrochloric or sulphuric acid, the case is quite different. These acid vapours are brought down by the falling rain, and this acid rain dissolves the oxide and exposes a fresh surface for oxidation; the new film is washed away by the next shower, and so on continuously. One of our greatest manufacturers of soda told me of a striking case of this sort. A shed in the midst of his works was thoughtlessly roofed with zinc. In the course of a few weeks it was fairly stripped, and the sheets of zinc were hanging down in ribbons. Similar

experience on a slower scale is common enough in Birmingham, where a builder, whose chemistry is at fault, uses zinc roofing in the neighbourhood of brass foundries, where 'pickle acqy' (i.e., the crude nitric acid used for dipping brasswork) is largely used.

Lead is preserved by an analogous but rather different action. In the first place, lead is less easily oxidised than either zinc or iron; still a film of oxide does form on a bright surface. When, however, there are any sulphides or sulphates in the air, this is soon exchanged for a sulphur compound. We do not find that lead turns yellow or red by becoming encrusted either by litharge or minium (red lead), its two oxides, but that it becomes either black or white. This film of sulphide or sulphate performs the same function for the lead as that of the oxide for the zinc, but is still more effectual on account of its greater insolubility. The action of sulphides on lead is strikingly shown in the City of London, where some of the old church spires are covered with sheet lead. These are uniformly black. This blackness is quite different from patches of black soot that engrime the stonework of the same buildings.

Bronze statues when newly cast are of golden hue, but after exposure become dark. This is chiefly due to the formation of a protecting film of sulphide, which acts as a preservative.

Let us now examine the action of air and water upon iron. As we all know, the iron is 'rusted' when exposed to ordinary atmospheric air. It is a rather curious fact, however, that in perfectly dry air iron and steel retain their brightness, and the same is the case when they are kept in water that has been completely freed from air. The necessity for such removal of the air will be better

understood by considering the fact that water dissolves a notable quantity of air. It is this dissolved or liquid air that fishes breathe. If it be pumped or boiled out the fish are drowned, just as we should be in ordinary water. But the air thus dissolved by water has not the same composition as that of the atmosphere, oxygen being more soluble in water than nitrogen. The dissolved air contains oxygen in the proportion of 1 to 2 by measure, instead of 1 to 4. Thus we have in the water a mixture of oxygen and nitrogen doubly as rich in oxygen as that of the atmosphere. The combined action of air and moisture appears to be necessary for ordinary rusting.

But what is this iron-rust?

The answer to this is not so simple as is commonly supposed. It is, of course, mainly oxide, but is it anhydrous or hydrated oxide, or which of the oxides of iron, and is there any carbonate or sulphide directly or indirectly concerned in the rusting process? These are questions of both philosophical interest and practical importance which, although they have been industriously studied as matters of pure chemistry, have received but little attention in reference to their bearing upon the practical problem of preserving iron from decay.

In order that what follows may be clearly understood, I will briefly describe the various oxides of iron and their hydrates in special reference to this subject.

First we have a questionable suboxide of iron, the black and somewhat malleable substance formed by burning iron wire in the oxyhydrogen blowpipe, and which, according to Marchand, invariably contains 6·79 per cent. of oxygen, and is, therefore, a compound of four equivalents of iron with one of oxygen, Fe_4O, or a compound of iron with its protoxide Fe_3, FeO, as it dissolves in mineral

acids with evolution of hydrogen. The small spherical shells formed in the familiar experiment of burning iron wire in oxygen has a similar, but less constant, composition. The same may be said of ordinary scale formed on the surface of iron in the course of its manufacture, the composition of which is still more variable.

We next come to protoxide of iron or ferrous oxide, FeO. This is the common oxide which is thrown down as a whitish grey hydrate, when alkalis are added to solutions of the proto-salts of iron. Although so common and so abundant, the chemist is unable to obtain a specimen of it. 'Not known in the separate state' is the best description that Gmelin can afford us in his unrivalled 'Handbook of Chemistry.' It is not only a very curious fact that a substance so continually before the chemist should so effectually evade his grasp, but this peculiarity also has a most important practical bearing upon the subject now before us. It is the master key of the whole mystery of iron rusting, as will be seen presently. Its intangibility results from its instability, and mainly from its ever-active propensity to take up more oxygen and pass into the state of the oxide next to be described.

This bears the various names of peroxide, sesquioxide, and ferric oxide. It exists abundantly in nature, both in the hydrated and anhydrous condition: anhydrous in red hæmatite, specular iron, martite, &c., and hydrated in the brown hæmatites, and many other brown iron ores. The hydrate is the main constituent of ordinary iron rust. An artificial hydrate is readily obtained by adding an alkali to solutions of the persalts of iron. It is then thrown down as a reddish-brown precipitate (*crocus martis aperitivus*). This, when strongly heated, is converted into the

rouge (*crocus martis adstringens*), which is artificial anhydrous ferric oxide.

There is something almost human in the inconsistent proceedings of the two principal oxides of iron. The ferrous oxide is continually struggling to obtain more oxygen and become ferric oxide, and then, when it has satisfied this ambition, it treats its acquisition with such indifference that it will give up a portion of its oxygen with the utmost readiness, especially when in the hydrated condition. Thus, the ferric oxide and ferric hydrate are very efficient and much used oxygen-carriers, or oxidising agents, while the ferrous oxide and ferrous hydrate are effective reducing agents, or oxygen abstractors, and are used by chemists accordingly.

When the two oxides or the two hydrates are in contact, we have a very complex series of giving and taking going on between them, resulting in the formation of what has been called *ferroso-ferric oxide*, or *scale oxide*. When iron is made red-hot, two or three distinct layers of scale are formed. The outer one is an approximate ferric oxide, the inmost is an approximate ferrous oxide, and the middle is a variable ferroso-ferric oxide of intermediate composition.

In like manner, if we mix the grey ferrous hydrate with the red-brown ferric hydrate, we obtain a very dark, almost black, intermediate hydrate, which, on exposure to air, gradually absorbs more oxygen, and becomes ferric hydrate.

Besides these, it is possible to form a definite compound of ferrous and ferric oxide, Fe_3O_4, which is found abundantly in a native state, and is therefore described in Chapter II. as one of the ores of iron.

There is another and higher oxide, called ferric acid,

FeO_2, which needs no description here, as it does not appear to perform any part in the natural decay of iron.

I must add that a carbonate of iron is readily formed by atmospheric action, but it is converted into ferric hydrate by further exposure, and also that when a sulphide is formed it is decomposed in a similar manner.

With these data before us, the practical importance of which will presently be seen, we may now be able to understand the anomalous action of the atmosphere upon iron surfaces, and grasp the principles upon which any successful attempts to remedy the mischief must be founded.

We must remember that, besides the mixture of oxygen and nitrogen which forms the bulk of the atmosphere, and the aqueous vapour it holds, there is always a certain amount of carbonic acid. As already stated, both iron and steel may be exposed to the action of dry air alone, or pure water alone, without losing their metallic lustre, and even in pure dry oxygen compact iron—i.e., iron in the state of ordinary lumps—remains unaffected at ordinary atmospheric temperatures.

It is very probable that the rusting of iron, by exposure to the air, is considerably aided by the carbonic acid of the atmosphere; at any rate, the first action is the formation of a protoxide, or a mixture of hydrated protoxide and carbonate. These, as already stated, readily combine with more oxygen and form the hydrated sesquioxide, or iron rust.

Let us now consider what will happen to a piece of iron thus covered with a thin coating of this sesqui-compound. Will it act like the film of oxide on the zinc, and protect the iron below from further oxidation? Experience answers, 'No,' and the properties of the oxides above described show us why not. The sesquioxide, especially

when hydrated, is a very effective oxygen-carrier. Many substances, when fairly exposed to its contact, oxidise more readily than when directly acted upon by gaseous oxygen.

Such, then, is the fate of the surface of metallic iron underlying the first film of rust. Instead of protecting the metal below as a stable oxide might, it actually oxidises it more rapidly than the air itself is capable of doing. It is not basic like the oxide of zinc, but it seems to act corrosively like a weak acid. It thus forms a protoxide or hydrate—this again passes into the state of hydrated sesquioxide, which again repeats its action on the iron below, and thus under some circumstances a thick piece of iron may be rusted bodily throughout.

The fact that the coating of iron rust is not compact, does not form a continuous film like that of the zinc, but is granular and porous, further assists the penetration of the oxygen, which is thus enabled to reach the inner film of protoxide, and to convert it into sesquioxide, which then proceeds with its deeper action.

I have said that the carbonic acid of the atmosphere probably assists in the ordinary rusting of iron, and also that the sesquioxide appears to act like a feeble acid. These inferences are suggested by the fact that the presence of alkalis, or other strong bases, prevents the oxidation of iron. Thus, if one measure of a saturated solution of potash is added to 2,000 measures of ordinary water, and a piece of bright iron be placed in this liquid, the iron retains its polish for months; but if the dilution is carried to the extent of one in 4,000 or 5,000, the protective power of the alkali is lost. If the water is previously saturated with carbonic acid, the addition of one part of the saturated alkaline solution to 1,000 of the

water is insufficient to prevent rusting. If carbonate of soda is used, one measure of saturated solution to fifty-four of ordinary water is necessary to prevent rusting. One in sixty is found to be insufficient.

There is a peculiarity in the action of carbonic acid upon iron which, if I am right in supposing that a carbonate is formed in the first stage of rusting, must materially assist in the penetration of the rust. It is this: When hydrated ferrous carbonate is exposed to the air or other oxidising agent, it abstracts oxygen, gives out carbonic acid, and gradually becomes converted into the ferric hydrate, or ordinary red rust. Thus, not only the hydrated sesquioxide is capable of giving off oxygen to the underlying iron, but even the carbonate, in the act of further oxidation, may, by the carbonic acid it evolves, contribute to the corrosion of the iron it covers.

Iron is thus an exceptional metal, one which, instead of obtaining protection from the film of oxide formed upon it, is actually subjected to a secondary oxidation by its own oxide, which has more powerful corrosive action on the metal than atmospheric oxygen, or even pure oxygen gas, undiluted with nitrogen.

I use the terms 'hydrated sesquioxide' and 'hydrated ferrous carbonate' to describe the rather indefinite compound of oxygen, iron, and water, and of carbonic acid, iron, oxygen, and water, that are concerned in these reactions.

Does sulphur protect iron as it protects lead, bronze, &c.?

Evidently not, for sulphides, sulphites, and sulphates, are sufficiently abundant in the atmosphere of our towns where coal is used for fuel; and we know that the rusting of iron proceeds even more rapidly in such places than in the open country.

An examination of the properties of the sulphur compounds of iron reveals the *rationale* of this. The sulphate being readily soluble cannot help to preserve the iron, as it would be at once washed away, like the copper sulphate from a copper surface.

But will the iron sulphide behave better, like the sulphide of copper, and of some of its alloys?

Again, our answer is, 'No,' for it is well known that sulphides of iron, when exposed to air and moisture, readily oxidise, and become converted into sulphates and sesquioxide. The manufacturer of Nordhausen sulphuric acid avails himself of this property by exposing roasted pyrites in heaps to the action of air and moisture, thereby obtaining the 'green vitriol' from which his acid is distilled. In the washing of coal slack the same occurs. The main purpose of this operation is to remove the yellow crystals and plates of iron pyrites (a compound of sulphur and iron). This compound, as is well known to those practically familiar with such coal washing, becomes, when heaped, gradually converted into sulphate of iron, or 'green copperas,' the soluble crystals of which are collected and sold where the washing is economically conducted.

Thus the formation of a sulphide on the surface of exposed iron is followed by further oxidation into soluble sulphate and more rust.

Before discussing the possible remedies, it is desirable to examine the mechanical and chemical conditions which accelerate the rusting of iron, and those which, on the other hand, assist in its preservation from destructive atmospheric action.

I have already stated that '*compact*' iron remains unaffected when exposed to dry oxygen at ordinary temperatures. If, however, very finely powdered iron (such as is

obtained when the oxide is reduced to the metallic state by hydrogen) is exposed to oxygen gas, it combines with such energy as to burn quite vividly. It takes fire spontaneously when exposed to the atmosphere at a temperature a little below that of boiling water. This indicates very strikingly the great influence of merely mechanical conditions of surface, and would lead us, *à priori*, to expect that if two pieces of the same iron, one with a smooth, a polished, or, better still, a burnished surface, and the other with a rough surface, were similarly exposed, the rough piece would be oxidised the most rapidly. This inference depends on the fact that, if we examine a rough surface, it is found to be made up of small granular or linear elevations and depressions—*i.e.*, it presents a number of small particles to the action of the atmosphere, instead of the comparatively continuous surface of the smooth, polished, or burnished iron.

Experience fully confirms this expectation, as may be seen by the examination of any old and exposed iron structure that has variable surfaces. The old railings round St. Paul's Cathedral (which are made of remarkably pure old English charcoal iron) display this difference in a very interesting manner. Bonsdorff tells us that iron remains unaltered, even in damp air, provided no water is deposited upon it, as when placed under a bell-jar, closed at bottom with a water-joint, and having a piece of tarnished lead likewise placed under it; the water is then exclusively deposited upon the lead. But if there are cracks in the iron, and these cracks filled with scale oxide, water becomes deposited upon this oxide, and rusting takes place. This action of roughness, or the exposure of minute angular protuberances, is by no means peculiar to iron; it is well known to favour almost all kinds of chemical action.

The influence of the ordinary chemical impurities of iron upon the rate of its rusting is considerable, and sufficiently interesting and important to demand special examination of the action of each.

First, as regards sulphur. We may safely conclude that it accelerates the rusting of iron, and its mode of action is probably that which I have already described as occurring when a film of sulphate is formed.

Phosphorus appears to have the contrary effect. Phosphide of iron resists oxidation with considerable stubbornness, even when mineral acids are called in aid. It dissolves but slowly in the strongest nitric acid or *aqua regia*, and is not attacked at all by dilute solutions of these acids, nor by cold sulphuric or hydrochloric acid.

Carbon also exerts a protective influence, the purest soft iron rusts more quickly than mild steel, this more quickly that hard steel, and soft cast iron more quickly than hard cast iron.

I am not able to say how manganese acts, whether it retards or accelerates the rusting of iron. When an alloy of iron and manganese is exposed to oxidisation at high temperatures, the manganese is the first to oxidise, and the known properties of manganese justify the theoretical anticipation that its alloy with iron should be more susceptible to atmospheric influences than pure iron, though it would be rash to depend too positively on this, as many alloys exhibit properties rather contradictory to the theoretical anticipations which are suggested by considering the properties of their constituents.

The action of silicon upon the superficial stability of iron is especially important. Silicon is very susceptible of oxidation at high temperatures, but, like carbon, is not oxidised at ordinary temperatures, and is little, if at all,

affected by moisture. The relation of its oxide to the corrosion of iron is diametrically opposite to that of sulphur. Sulphuric acid applied to the surface of iron oxidises and dissolves it, while silicic acid forms an insoluble superficial enamel, which is the most effective of all known preservatives. Cast iron containing much silicon is, of all the common varieties of iron, the one that rusts the most slowly.

This protective action of silicon, phosphorus, and carbon presents a contradiction which is not only curious, but of considerable practical importance. It teaches us that some qualification is necessary in describing iron as good or bad, as it shows that iron which is the worst as regards toughness, is the best when judged by its power of resisting corrosion; that when iron is to be used for the purpose of mere superficial covering, the worst quality, as usually described, is really the best.

An instructive example of this contradiction occurred in the course of my own experience at the works of Sir John Brown and Co., Sheffield. The armour-plating of a Spanish ship of war was in course of preparation, and the bolts were to be galvanised. This was an unusual demand, and the galvanising process was but imperfectly understood at the works. The zinc was melted in an iron bath of suitable dimensions, and the bolts dipped into it; but it was found that the bath itself rapidly corroded, and its continual renewal was attended with considerable expense. I was consulted, and found that the foreman superintending this work had naturally sought to obtain the greatest possible durability of the bath by making it of the very best boiler-plate. An examination of one of the old baths at once revealed the cause of the mischief. The zinc had 'galvanised' the bath, not merely on its surface,

but had penetrated it throughout, forming with the iron a fusible alloy, and hence the 'burning out,' as the workmen called it, of the bottom.

I suggested that, instead of using the best wrought iron plates and riveting them together, that the bath should be cast from the worst sample of pig-iron that could be found in the works. This suggestion appeared so absurd and contradictory, that it was not without considerable difficulty and delay, and some pressure, that I could get it carried out. The result was quite successful. The cast bath, made from bad iron, lasted above six times as long as the wrought bath made from the best boiler plate.

The difference was mainly due to the protective action of the silicon. It is well known that when iron is dipped in melted zinc or tin, for the purpose of galvanising or tinning, the presence of a little cinder on any part of the surface, prevents the melted metal from adhering. This is due to the glassy silicate of iron, which is incapable of amalgamating or alloying with zinc or tin. It resists oxidation in a similar manner.

This subject is worthy of careful consideration, for 'bad iron,' especially that containing much phosphorus and silicon, is easily made in certain districts; and it cannot fail to be satisfactory to manufacturers to learn that there may be many purposes for which it is really better adapted than purer and dearer iron.

Having examined the chief causes of surface-corrosion and their mode of action, the means of preventing or diminishing such deterioration may now be considered. What I have already stated concerning the influence of the composition of the iron itself directly suggests, that, where great tenacity and toughness are *not* demanded, an

iron containing a considerable proportion of silicon, carbon, and phosphorus is preferable to iron of greater purity, provided always that it contains but little sulphur. The presence of much sulphur would probably neutralise the protective action of the other impurities, and I suspect that this has prevented the superiority of 'bad iron' for certain uses from becoming practically understood. Every practical iron-worker can distinguish between ordinarily pure iron and that which is much less pure, but there are but few who are able to determine the source of the impurity.

I strongly recommend the manufacturers of some of those brands of Cleveland pig which are comparatively free from sulphur, but are much depreciated in value on account of the phosphorus they contain, to make similar castings from theirs and higher-priced irons, and, by exposing them equally to atmospheric action, compare the rate of corrosion of each.

If my theoretical anticipations are sound, the result of such trials will prove the superiority of these siliceous irons for many important purposes, such as cast water-pipes, spouting, many kinds of ornamental work, &c.

The most obvious device for defending iron against surface-corrosion is the coating it with some kind of adherent film, which is more or less capable of resisting atmospheric action. There are two distinct classes of such coverings—first, those which are dissolved in some liquid, are applied cold, and slowly solidify by evaporation or chemical change; and second, those which are fused, are applied hot, and solidify on cooling.

Of the first class the most common are paints and varnishes. These are so numerous that a separate examination of each would form a chapter in itself. I must,

therefore, refer only in general terms to the properties of the most important.

A paint consists of two chief components, the liquid *medium* and the solid *body*, the body being intimately mixed, but not dissolved in the medium. Thus, in ordinary white paint, the body is carbonate of lead or 'white lead,' and the medium is linseed oil alone, or more commonly a mixture of linseed oil and turpentine. Turpentine is a volatile oil, *i.e.*, one of those oils which, when pure evaporate away so entirely that if a piece of paper is wetted by them, and then exposed to the air, no film or stain is left behind. Therefore, if the body were mixed in pure turpentine, the paint would be worthless, as on drying the body would be left behind as a mere dry powder that could be readily brushed away.

The use of the turpentine is merely to dilute the linseed oil which is the true binding medium, and to hasten the drying, the paint being thinned or weakened in proportion to the quantity of turpentine that is used. It is important that this should be clearly understood by all who use ordinary paint for the protection of iron.

Linseed oil is quite different. It is a fixed oil, *i.e.*, it does not pass away by evaporation at ordinary temperatures, it cannot be boiled away nor distilled by heating it under ordinary atmospheric pressure, because its boiling-point under such pressure is higher than its dissociation-point, or the temperature at which it is decomposed by heat. But it does dry somehow; in this drying property it differs from ordinary fixed oils, such as olive oil, &c., and thus belongs to another subdivision of the fixed oils, viz., the 'drying oils.'

How, then, does it dry if not by the ordinary process of evaporation, such as effects the drying of water, spirits, volatile oils, and most other liquids?

This question is answered by the fact that it contains about 80 per cent. of a very curious liquid to which the name of *linoleine* has been given. This linoleine, when exposed to the air, slowly combines with oxygen, and is thereby converted into a solid substance of translucent resinous appearance, and possessing much of the toughness and elasticity of india-rubber or gutta-percha, though long exposure to light and a moderate degree of heat, such as that of the sun's direct rays, renders it harder and rather brittle. It is adhesive, remarkably impervious to water, and very difficult of solution either in essential oils, spirits, naphtha, or even bisulphide of carbon. Another important and valuable property of this linoleine is that it *expands* in drying. This expansion is a simple result of its combination with oxygen, which increases both its weight and bulk. The difference between a varnish and a paint may now be understood as it should be, for the distinction is not merely theoretical but has some important practical bearings.

In varnishes the solid or body is *dissolved* in the medium, and the drying (with one or two exceptions, where a drying oil is the solvent) is effected by the evaporation of this medium. Gums, resins, or those intermediate vegetable products called 'gum-resins,' usually constitute the soluble solid of varnishes, and the medium is a volatile oil, spirit, or similar liquid. The solution forms an unctuous adhesive liquid which, when spread out, becomes, on drying, a solid resinous film.

It will be seen from this that there is a remarkable difference between the drying of a paint having the linoleine of drying oil for its medium, and the drying of a varnish, the medium of which is volatile, and dries by evaporation. In the latter there is a loss and *shrinkage* in

drying; in the case of the linoleine there is a gain (of oxygen) and an expansion. The importance of this, where the object is the protection of iron from corrosion, is very great, for the *shrinkage* of the resinous film of the varnish is liable to destroy its continuity, and form minute cracks through which atmospheric agents may reach the iron. This tendency to cracking is increased by the expansion and contraction to which metals are subject from variations of temperature. The thicker the layer of varnish the greater is the liability to cracking and peeling.

The reader, who is well versed in metal work, will probably object to this by quoting the common and successful use of a true varnish—viz., solution of gumlac or shellac in alcohol—for the lacquering or preservation of brass. But this same lacquer affords so little aid in the preservation of iron, that, although it may be easily applied, it is very rarely used for the purpose of preserving iron or steel. This, I suspect, arises from the peculiar insinuating character of the oxidation of iron, due, as already explained, to the fact that the iron rust itself acts as an oxygen-carrier. Every crack, pore, or other flaw in the varnish, however small and invisible to the naked eye, becomes a centre of corrosion, from which the oxidation spreads downwards and radially, undermining all around. This undermining of the film is the more effective from the fact that the rust occupies a much greater bulk than the iron itself, and thus in swelling it must uplift and peel off the brittle film of shellac or other varnish, by a sort of microscopic eruption.

This inward spreading and undermining action of iron rust is the main source of the difficulty of protecting it by paints or varnishes. Even the continuous linoleine film, in spite of its compactness and the increased substan-

tiability afforded by the body of the paint, gradually loses its toughness, curls up and peels off, revealing below a stratum of oxide which has somehow formed in spite of it. I think it quite possible that the fully oxidised linoleine may give up some of its oxygen to the iron surface which it covers. This idea is, however, purely speculative, as the subject does not appear to have been directly investigated.

The mechanical adhesion of the protecting film is, of course, a matter of primary importance. Certain substances are said to be '*sticky*,' and such adhesiveness is very commonly regarded as an absolute quality. This is a great mistake. The adhesive affinities of any substance, whether solid, liquid, or gaseous, vary according to the second body with which it comes in contact. If we take a common pair of scales, balance them, and then allow one of the pans to touch the surface of the water in a saucer, we shall find that it adheres to the surface of the water with considerable force. This force may be measured by gradually adding weights to the other pan until the adhesion gives way, and the beam is tipped in the direction of the weighted pan. By varying the experiments and using flat discs instead of the pan, we may learn whether water adheres with equal or varying force to different solids.

The discs may be of, say, iron, steel, copper, tin, zinc, silver, brass, glass, &c.: if all are of the same shape and of equal size, and balanced before touching the water, the weight required respectively for effecting their detachment measures their respective forces of adhesion. These will be found to be curiously different. If we now acidulate the water, then make it alkaline, afterwards substitute it by alcohol, oils, ether, mercury, &c., we shall with each substitution obtain a new set of relative adhesive powers

for each of our solid discs. The most remarkable differences will be found in comparing the adhesion of mercury to iron with that to such metals as lead, tin, copper, &c.

Similar variations occur in the power of adhesion of the different films of which paints and varnishes may be composed, and it must be understood that in painting or varnishing a metallic surface it is the adhesive force, pure and simple, that we have to depend upon. In painting wood or other porous material the adhesion is aided by the fact that the paint penetrates the pores, to a greater or less extent, and these extensions inward form minute rootlets by which the film is the more firmly held. If the film swells in drying, as in the case of the linoleine, these roots become firmly wedged, and the paint is almost irremovable.

The practical question before us now assumes a definable shape. It becomes: What available film has the most complete continuity or least porosity, and the strongest adhesion to iron, and is at the same time insoluble and impenetrable by the vapours and gases of the atmosphere? Here is a large and fruitful field for investigation, and one which has never been systematically tilled. We have only the random results of isolated, conflicting, and ill-recorded experience to guide us.

If I may venture to express an opinion founded on my own observation, which I do with much diffidence on account of its limited and desultory character, I should say that pitchy or bituminous films are especially effective as regards their adhesion to iron. Thus a solution of asphalte or pitch in petroleum or turpentine leaves a strong adherent film on drying. It is also very effective as regards its continuity, on account of its manner of drying. Instead of forming a hard and brittle scaly film,

like most of the gum resins, the pitch film retains a certain degree of plasticity which effectually prevents any cracking, and permits a yielding with the contraction and expansion of the iron. If the iron is at all rusty it penetrates the spongy surface of oxide and envelops the rust-particles very effectively, holding them together and enlisting their services to form a portion of its paint-body. Such a solution of pitch or asphalte may be regarded as something between a paint and a varnish, the pitch or asphalte being a resinous substance, and, therefore, by its solution forming a varnish; but it is not a pure resin, for it contains, and is coloured by, minute solid particles of carbon, and these, of course, when diffused through the solution, correspond to the body of a paint.

Against these advantages there is one serious objection to a mere solution of pitch. It is to a certain extent soluble in water, and thus when exposed to rain the bituminous film is gradually washed away. This, however, may be remedied by mixing the solution of bitumen with linseed oil, or with a thin paint made by grinding red or white lead in linseed oil. I have tried this; I find it stand very well, and the experiment may easily be repeated by mixing about two parts of Brunswick-black with one of ordinary white, red, or stone-coloured paint, the body of which is composed of red or white lead, or litharge.

There are many kinds of bitumen that may be used, such as natural mineral asphalte, pine-pitch, and artificial asphalte. There are two distinct varieties of the latter, differing materially in their properties. The first and most common is that which is left when the dead oil, &c., are distilled from common gas-tar; the second, the residue which is left when the spirit, lamp oil, lubricating oil, and solid paraffin are incompletely distilled from petroleum,

or from the crude oil obtained by the distillation of cannel coal or bituminous shale. It is this which I recommend. It is easily obtained, and may be supplied in abundance from the neighbourhood of Bathgate, by the Scotch manufacturers of mineral oil. In order to obtain it in suitable condition for this purpose, the crude oil must be distilled before treatment with acid, and the final distillation stopped before the coking point is reached. By this means a hard, bright pitch is obtained which contains a considerable body of carbon, and which is soluble in the unrefined or 'once run' paraffin spirit, which itself is a mere drug in the market, and may be supplied at a very low price. Where small quantities are required the refined spirit which is used for sponge lamps, and commonly sold under the name of '*benzoline*,' may be used. It is nearly the same, but a little dearer.

When I was engaged in distilling cannel at Leeswood, in Flintshire, I prepared a quantity of such paint, and used it very successfully for the preservation of both iron and wood. For such purposes as painting the hinges of cucumber frames, the hoops of water-barrels, &c., I used it mixed with only a little boiled linseed oil, and without any further body than the pitch contains. When this sort of bitumen, which for distinction sake I will call *paraffin pitch*, is obtainable, no further admixture than about one-half or one-third of its bulk of boiled oil to the solution in spirit is required.

Another experience of my own may be recorded, as it is instructive.

About 20 years ago I was consulted respecting the means of cleaning and preserving a collection of very choice specimens of ornamental mediæval ironwork, intended for presentation to the Sheffield Technological Museum by

the late Mr. William Bragge. They had been somewhat neglected, and were already rusted. The problem to be solved was to remove the rust without damaging the surface, and to prevent further corrosion, without destroying the metallic tone of the surface or obliterating the sharpness of the fine ornamental work. The rust might have been at once removed by oxalic acid, but this and all other acids penetrate iron to a certain depth, and afterwards set up a new corrosion, however carefully they may be wiped or washed away. Therefore, the use of any acid would have been ruinous. Painting over the surface in the ordinary way would have been downright Vandalism, worse than the churchwarden's mode of cleaning cathedral stonework by whitewashing it. Ordinary oiling had been tried, but, though preferable to either of these, was not satisfactory. What, then, was to be done?

I obtained from a friend in Flintshire a sample of 'once run' mineral oil—*i.e.* paraffin oil that had been redistilled from the crude oil, but not yet washed with sulphuric acid. This oil contains sufficient free carbon to stain it with a brown tinge, but the particles of this carbon are so infinitesimally fine that their solidity is questionable—they may be regarded as carbon in actual or semi-solution.

This was sent to Mr. Bragge's brother—an amateur artist—who had charge of the specimens, with instructions that it should be first brushed smartly over the surface of the iron until all the rust disappeared, then wiped off and a second brushing applied lightly, and the surface left slightly and uniformly wetted with the oil. These instructions were ably carried out, and the result is reported to be very satisfactory. The rust was removed without violence; the rusted parts regained their natural colour

when wetted with the oil, and retained it after the oil dried. As the minera oil is slowly volatile, this drying took place gradually, an imperceptible film, due to the semi-dissolved carbon, remained behind, and protected the iron from further oxidation, without in any degree damaging the tone of its surface. It will, of course, be understood that so delicate a film as this is only fitted for defending the iron from that degree of corrosion to which such carefully-preserved specimens are liable. It has the advantage of being very easily applied, and may be repeated with any degree of frequency without damage, as each fresh brushing removes the previous film, as well as any rust or dirt that have subsequently invaded the surface.

Since this the use of paraffin oil for cleaning iron and steel has become common, but the superiority of the 'once run' to the ordinary refined oil, in the refining of which strong sulphuric acid is used, is by no means sufficiently understood.

Before leaving the paints and varnishes, a few words are due to a very humble and vulgar, but by no means uninteresting mode of protecting iron surfaces, viz., the housemaid's device of 'black-leading.' In these days of general diffusion of chemical knowledge, it is scarcely necessary to state that the 'black lead' or 'plumbago' of commerce is not lead at all, nor any compound of lead, that it includes no lead whatever in its composition. Neither is it a carburet of iron, as is sometimes stated. It is simply carbon; pure plumbago is pure carbon, impure plumbago is impure carbon. Its proper name is graphite—*i.e.* writing-stone. I may venture to describe it as the softest of all true solids, and have often pondered wonderingly upon the apparently unnoticed, but very curious chemico-mechanical

paradox, that the hardest and softest of all the solids existing upon this earth are, chemically speaking, the same substance; graphite and the diamond being both carbon.

It is this wonderful softness, combined with persistent solidity, that enables us to smear it over any other solid surface, and thus obtain a *solid paint*, all body and no medium. For the class of castings to which it is commonly applied, where its application can be readily repeated, and where it is not exposed to the direct action of water, it is unrivalled as a protecting film to iron. Its chemical action, so far as it does act when cold, is reducing or anti-oxidising. Its film is so marvellously thin that when properly applied it obliterates nothing. I have never met with any attempt to estimate the thickness of a well-brushed film of graphite, but I suspect that if a hundred strata of such films could be piled in actual contact with each other, their combined thickness would fall short of that of the thinnest gold leaf. This estimate is based upon what I have observed in using it for purposes of electro-deposition. The chemist, therefore, can give but little aid to the housemaid in this matter, he can only explain and admire her practical discovery.

The application of protective films by means of fusion next claims attention. Tinning, and the process to which the absurd name of 'galvanising' has been applied, are the most prominent of these. The principle and practice of the mode of application is the same in both, though the material of the protecting agent is different, zinc being used in the place of tin for the latter process.

In both cases the iron surface is made chemically clean. This is effected by the combined action of mechanical scrubbing and chemical 'pickle.' The pickle used is hydrochloric acid for galvanising, and the same with or

without a second pickle of sulphuric acid for tinning. The iron thus cleaned is either dipped in a bath of melted tin or zinc, or the melted metal is brushed over it. The dipping is the best, and is used where applicable, care being taken to brush or drain off the excess of adherent fused zinc or tin. It would be out of place here to describe the many precautions necessary to conduct these processes effectively and economically. A considerable amount of skill is demanded, especially in tinning.

This demand for skill, as well as the effectiveness of the protection afforded to the iron, depends on the fact that the tin or zinc is not merely painted over the surface of the iron, but that an actual alloy or amalgam is formed, which extends to some depth below the surface. This is shown by placing a thick piece of iron in a tinning or galvanising bath, leaving it there for some time, and then breaking or cutting it through. The fracture or section shows that the zinc or tin has penetrated to a measurable depth below the surface, and this depth increases with the time of immersion; thus it is very easy to tin or galvanise a piece of iron completely throughout. Such a piece, on being filed or otherwise worked, presents all the appearance and properties of a true alloy.

In the ordinary course of tinning and galvanising, the cost of the tin and zinc, especially the former, being considerable, the iron is only immersed sufficiently to ensure a complete surface covering, with as little penetration or internal alloying as possible. This fact seriously limits the value of this mode of protecting iron. As we all know, both tinned and galvanised vessels used for containing water begin to rust after a certain length of time, and as the skill of the tinner in economising of material increases, the durability of his work diminishes.

I think that some of our enterprising manufacturers would do well to consider whether it would pay to bring out a new class of tinned and galvanised goods, the tin or zinc of which should be guaranteed to have penetrated bodily through the iron. For many purposes this would be very desirable. Such an alloy would be almost imperishable. As zinc is so much cheaper than tin, and appears to penetrate iron more readily, it is in the direction of galvanising that this suggestion might be more readily carried out.

The influence of such a soaking of iron and steel with a foreign metal upon its tenacity suggests a very interesting subject for investigation. Is the metal of inferior tenacity so alloyed or combined with the more tenacious iron as to form a compound of intermediate tenacity? Or does the penetrating metal merely soak itself into the pores of the iron or steel and thus solder together the fibres, crystals, or granules and increase their tenacity? These are fair questions, and worthy of experimental reply.

The protective effectiveness of tinning and galvanising is unquestionable, but their applications are necessarily limited to small ironwork and utensils. Structural iron can receive but little aid from them. Another limitation is due to the fact that iron of very superior quality and unblemished surface is required. For tin plates charcoal iron is commonly used, and even this is subject to failure from the accidental presence of cinder on the surface of the plate. All plates and sheets rolled from puddled iron are subject to this defect, however great may be the care that is used in their manufacture.

In 1868 I sent to Messrs. Griffiths & Browett, of Bradford Street, Birmingham, some sample sheets rolled from Bessemer steel, and carefully annealed under my own

supervision. The object was to test the fitness of such material for the 'hollow-ware' so largely manufactured by this firm, especially when used for articles—such as dish covers, &c.—that are tinned after being shaped. As this cast material is not liable to cinder patches on the surface, the trouble above referred to is escaped.

The experiment was successful, and Bessemer sheets are now in common use for tin-plate making. I have specimens of vases hammered and 'spun' from a flat piece of metal, showing by this remarkable change of shape that such material may, by proper annealing, be made as soft and tough as charcoal iron.

There is another mode of protecting iron, viz., by coating it with lead by means similar to those used in tinning and galvanising. Such leaded iron is utterly unfit to supersede tin-plate for culinary utensils, as all soluble compounds of lead are poisonous, are the most treacherous of poisons, as they act by gradual accumulation. The danger is increased by the fact that acetic acid, or vinegar, dissolves lead so readily, and this acid may be formed accidentally by the fermentation of substances commonly used for food.

For many purposes, such as roofing, spouting, &c., wherever zinc is commonly used as a substitute for sheet lead, this leaded sheet iron may be very useful, and I think deserves more attention than it has yet received. I used it successfully at Leeswood, in Flintshire, for the construction of condensers attached to retorts, in which cannel and shale were distilled for their liquid and solid hydro-carbons. These condensers were upright cylinders standing out in the open air, and cooling by radiation.

Many attempts have been made to protect iron by electro or chemical deposition of copper and its alloys.

When electro-depositing was a new invention, several patents were secured for this idea in its crudest form—viz., the precipitation of copper on iron from acid solutions. All these have utterly failed; the copper peels off, leaving a surface of iron far more corroded than if no attempt at protection had been made.

Some interesting investigations, made by Mr. W. H. Johnson, of Manchester, on 'The Influence of Acids upon Iron and Steel,' afford a clear explanation of this. He finds that acids not merely attack the surface of iron, but rapidly penetrate it, and, like the tin and zinc above referred to, can be detected within the iron when a fracture is made. He finds that acids which have thus penetrated not only continue their corrosive action, but, aided doubtless by the hydrogen evolved and occluded, they seriously diminish the tenacity of both iron and steel.

All who have practically investigated this subject of coppering and brassing iron agree in concluding that if the liquid in which the copper or alloy is dissolved is of itself capable of acting corrosively on the surface of iron, no reliable adhesion of the precipitated copper or brass is possible. By using neutral or alkaline solutions, such as those in cyanide of potassium, an adherent film may be obtained; but even this is not satisfactory, the copper, especially when moderately thick, being very liable to 'buckling.' This tendency is, I suspect, in a great measure due to the unequal expansion of copper and iron. When raised from 32 to 212 degs. Fahr., copper increases in bulk $\frac{1}{194}$, or in length $\frac{1}{582}$, while iron increases only $\frac{1}{282}$ or $\frac{1}{846}$, or, otherwise stated, the expansion of copper when heated, and its contraction in cooling, is nearly one and a-half times greater than that of iron. This is a very serious difference, and its practical operation must be the

exertion of a continual tearing strain between the two adherent surfaces.

I have tested the adhesion of many specimens of such coppered iron by directing the point of a blowpipe flame against a portion of its surface, and, what amounts to nearly the same, by burnishing a portion of the copper surface. In both cases an excessive expansion of the copper was produced, and a blister of the copper film was the result. These, of course, are very severe tests, especially the burnishing, which leaves a permanent blister.

Another defect arises from the porosity of such deposits. Although the pores may be invisible to the naked eye, they nevertheless usually exist, and are of sufficient magnitude to admit atmospheric agents, which act upon the iron surface with an energy which is intensified by the voltaic induction due to the electro-negative copper.

These defects have been to some extent remedied by first tinning or zincing the iron, and then depositing the copper on the alloyed surface, but the additional expense of this process limits very seriously its applicability, and leaves large masses of structural iron altogether out in the cold.

I must not conclude without some discussion of the merits of enamelling, even though its applicability is so obviously limited. If mere unchecked theorising were permissible on such subjects, it might be assumed that this is a really perfect protective process, the enamel itself being practically imperishable, in reference to corrosive atmospheric agency, and the iron basis affording to the porcelain surface just that tenacious core which its own brittleness demands.

But here again porosity and inequality of expansion

seriously limit the value of this theoretically beautiful process. The co-efficient of expansion of the vitreous compounds used for enamelling is about $\frac{1}{1000}$, against the $\frac{1}{846}$ of iron, and the brittleness of the enamel renders fatal even a very small difference of expansion or contraction. This is shown in the ruin that comes upon those apparently perfect and beautiful devices, the enamelled frying-pans, saucepans, &c. They chip and scale most vexatiously.

While I was engaged as the teacher of chemistry and its practical applications in the Birmingham and Midland Institute, an eminent Birmingham firm in the hollow-ware trade consulted me in reference to an improved process of enamelling that was offered for their adoption. The inventor was hardy enough to suppose that it might be applied to the manufacture of evaporating basins and other vessels, in which acids, &c., were to be heated. I devised a simple test which proved quite effectual, and which I venture to recommend for general use in such cases.

Some evaporating dishes were made, and I immersed these in a strong solution of sulphate of copper, leaving them there about twenty-four hours. The result was very disagreeable; a large number of small copper warts were dotted on the surface of the enamel, and were especially abundant on the edges of the dishes at the junction between the blue outside and white inside coating of enamel. Mere immersion in acid showed nothing unless continued for several days; but the deposition of copper in the minutest pores, and its outward cauliflower-like expansion, displayed at once those defects which would have become more vexatiously and mishievously apparent in the course of time, had large vessels been made and practically used.

If any enamel stands this test, I think it might be safely warranted for ornamental and other purposes, where the enamelled articles are not exposed to great fluctuations of temperature.

A perfect, or at least satisfactory, and generally applicable method of preserving iron, has yet to be invented. I do not think that the problem is by any means insuperable, for the principle upon which its solution must be based can be clearly stated, and this is an important step towards effecting it. We require something which may be applied easily over large or small surfaces, like a paint, varnish, or lacquer; but it must not be paint, nor a varnish, nor a lacquer; it must be no mere heterogeneous film holding on by mere mechanical surface-adhesion; it must be chemically attached to the iron, as their sulphide and sulphate films are attached to bronze and lead.

What I have already explained respecting the protective action of the compounds of iron with phosphorus, and with silicon or silica, affords fair indication of the direction of research. The ordinary enamels are vitreous compounds of foreign metals fused over the surface of the iron; what we require is to glaze the iron by vitrifying *its own surface*. The Protean solubilities of silicic and phosphoric acids obviously suggest the possibility of doing this without having recourse to fusion at high temperatures. Such a film of iron-glass upon iron would not deface or materially alter the natural appearance or tone of the metal. It would satisfy æsthetic as well as chemical requirements.

The above was written before the 'Bower Barff' process for protecting iron was introduced. It consists essentially in coating the metal with a film of black or magnetic oxide by exposing it to sufficient heat—with or without

the aid of superheated steam—to cause the formation of such superficial coating.

Having had no practical experience in the use of this, I am not able to give an opinion on its merits, beyond stating the fact that such oxide itself has remarkable power of resisting atmospheric action; but I cannot say whether or not the film formed by either of the patented processes is sufficiently continuous and adherent to effect the desired protection efficiently when applied to cover large surfaces, and thus exposed to the tearing action of unequal expansion.

CHAPTER XXI

THE OCCLUSION OF GASES IN IRON AND STEEL

In Chapter XVI. I referred, in passing, to this subject, and also in Chapter XIV., when discussing the rationale of cementation; but in order to fairly understand the phenomena and operation of occlusion, and the effects that have been attributed to it, a general view of the whole subject is desirable, especially as chemical combination and this mechanical or quasi-chemical combination are sometimes confounded, and very questionable theories evolved in consequence.

Everybody knows that gases are compressible. Until recently they were divided into two classes, the 'permanent gases' and condensible gases, or 'vapours.' Recent experiments, consisting simply of applying very great pressure in conjunction with low temperatures, have swept away this distinction by showing that the so-called permanent gases differ only from the familiarly condensible vapours in having a lower boiling-point; that all gases are but the vapours of certain liquids and solids, just as steam is the vapour of water and ice. The boiling-point of water at ordinary atmospheric pressure is 212 degs. Fahr. As this pressure is increased the boiling-point rises; as it is diminished the boiling-point falls.

Long ago Faraday showed that chlorine was not the permanent gas then described, but that it might be con-

densed to an oily liquid by pressure and cooling. This was one of his earliest discoveries, made when he was assistant to Sir Humphrey Davy, and the subject of a dispute between him and his employer, who sought to appropriate the honour of his assistant's work. Subsequently carbonic acid was similarly condensed to a liquid and to a solid, an experiment that has long been familiar at our lecture tables. But oxygen, hydrogen, and nitrogen still resisted, and appeared to be incondensible. Now, however, they have been unequivocally reduced to the liquid and even solid form. This has been done mechanically by simply squeezing and cooling them simultaneously. Oxygen has thus been liquefied, and the boiling-point of liquid oxygen shown to be 376 degs. below freezing (Fahr.). The boiling-point of nitrogen *in vacuo* is about 424 degs. below freezing. Snow-like crystals of solid nitrogen of considerable size have been obtained, and hydrogen has been similarly solidified.

These are results of artificial pressure and cooling applied from outside, the gases themselves remaining passive; but there is another case, in which the gases take an active part in effecting their own compression. They attach themselves to the surfaces of solids by an adhesive force, or 'attraction of adhesion,' as it has been called.

A good and pertinent example of this adhesion of gas to a solid is afforded by dusting a few iron or steel filings on the surface of water. Instead of sinking, as they should in accordance with their specific gravity, they float freely. The reason of this anomaly will reveal itself if the sprinkling is continued until several strata of the filings are piled one above the other on the surface, and the pressure of those above thrusts down the lower particles. The number of these, or the thickness of the

layer before it sinks, depends upon the fineness of the filings. When they have gone down, it will be seen that they are enveloped in a body of air. They usually agglomerate with the air visibly between each particle.

If the water be now poured off from them, they will be found to remain dry, even after a long immersion. Each particle had an obstinately adherent atmosphere of its own, forming a little balloon, which buoyed it up. The quantity of air thus adhering must be considerable. The specific gravity of iron being about 7½ times that of water, the bulk of the air adhering to the iron in order to buoy it up, must be more than 6½ times that of the iron—*i.e.*, 6½ times if the air itself had no weight.

A curious contrast to this floating of the iron is afforded by sprinkling on the surface of the water, in like manner, a little of the powdered calcined magnesia supplied as medicine. This powder is so fine and light that it falls very slowly through the air, but it descends at once in water, while the iron floats. The finest samples of magnesia fall more rapidly through water than through air. This appears to be owing to adhesion of water instead of air to the magnesia.

The difference thus displayed indicates that this adhesion of gases to solids, and of liquids to solids, is selective. Further experiment has proved this to be the case. Each particular solid has its own particular affections for certain gases and liquids, and they vary very greatly. Mercury poured on iron runs over it in little balls; but if poured on clean lead, or tin, or copper, or silver, or gold, it adheres at once, and spreads itself out upon the surface of the metal. This selective character likens adhesion to chemical attraction, and suggests at first glance a con-

nection with chemical affinity, but this idea is refuted by further investigation.

The particular gases that most readily and vigorously adhere to particular solids, are not those which combine with them the most readily. Thus the table on page 271, of the quantities of different gases condensed within the pores of a cubic inch of newly-burned box charcoal, shows that 90 cubic inches of ammonia are thus absorbed, 85 of hydrochloric acid, 65 of sulphurous acid, 55 of sulphuretted hydrogen, 40 of protoxide of nitrogen, 35 of carbonic acid, and 35 of bicarburetted hydrogen, neither of which has any perceptible chemical affinity for carbon; while of oxygen, that has so strong an affinity for it when heated, only 9 cubic inches are taken in. As we shall presently see, the metals behave similarly.

But some of my readers may, perhaps, object to the classification of the phenomena of condensation of gases within the pores of charcoal with that of the occlusion of gases in metals. They may base this objection on the visible porosity of charcoal and the apparent continuity of the metal. It may be well, therefore, to step a little aside in order to remove this objection.

As a matter of fact, the metals are curiously porous to certain gases, and this porosity is selective, and demonstrably connected with their occlusion of such gases. MM. Sainte Claire Deville and Troost have proved that hydrogen gas penetrates tubes of platinum and iron with surprising facility; and Professor Graham, in a paper read before the Royal Society, June 20, 1866, connects this permeability with the adhesion of the gas to the surface of the metals, and its occlusion by them, as in this behaviour they merely resemble other substances which are

permeated in like manner by gases which we cannot force through them by mere mechanical pressure.

India-rubber, which otherwise is so different from metals, is a good example. Through a thin film of this both oxygen and nitrogen pass, but, as Graham states—with good reason—not as gases, but by first becoming liquefied on the entering side, then passing through in the liquid state, as ether and naphtha do, and then evaporating from the other surface, or the emerging side, which is under the influence of a vacuum, while the entering side is freely exposed to the gas.

If common air be the gas on one side, it becomes curiously filtered: all its oxygen passes through, but only one-half of its nitrogen, the filtered gas thus obtained being so rich in oxygen, that a glowing wood match bursts into flame when immersed in it.

Chemical affinity is usually the most energetic when exerted between dissimilar bodies, or bodies having widely different properties; thus, acids and alkalies, which are typical chemical opposites, afford typical instances of chemical affinity; the energetic combinations of the metals are with the non-metals, the combination between the metals themselves being so tame, that alloys are rather to be regarded as mechanical mixtures than chemical compounds. Hydrogen, although a gas at ordinary temperatures and pressures, is chemically a metal, was regarded so before it was solidified, and now it appears in its solid form to further justify this classification.

It is this metallic gas, or gaseous metal, that displays the most remarkable phenomena of occlusion by other metals. Palladium surpasses all the other metals in the quantity of gas it is able to occlude—as much as 643 times its own volume, with so little increase of bulk that

the hydrogen must be in the solid form. Hydrogen, thus solidified and combined, has been named '*hydrogenium*,' in accordance with the usual rule of applying the termination *um* to the Latin names of metals. Graham regards the palladium thus charged with hydrogen as an alloy of the two solid metals, palladium and hydrogenium.

There is, however, one remarkable fact, the bearing of which on this theory he seems to have overlooked.

If the occlusion of the hydrogen were a filling up of the mechanical pores of the palladium, the greatest amount of occlusion shall occur in the palladium in its most porous condition. Every practical mechanic knows that metal simply fused and cooled is more porous than such metal after hammering or rolling. Graham found that palladium foil of hammered metal condensed as much as 643 times its own volume of hydrogen, while foil of fused palladium only absorbed 68 volumes. He says: 'A certain degree of porosity may be admitted to exist in these metals, and to the greatest extent in their hammered condition.' This, I think, is a mistake if he means mechanical pores. The effect of hammering is to close the pores, more or less, and condense the metal accordingly.

I would rather suggest a somewhat different explanation by supposing that the hydrogen is compressed by adhesion to the surface of the palladium, forming an excessively thin film, so thin that the walls of a pore of visible dimensions would be tinned, so to speak, on all sides, and still remain a pore; but a smaller pore, when similarly tinned or hydrogeniumed (to coin a hideous but correct and expressive word), would be filled with the hydrogenium, because the two surfaces of its film would join each other, and weld together if the depth of the pore did not exceed that of their united thickness.

The probability of this is increased when we consider the nature of the action of hammering or rolling. It flattens the pores, converts globulous pores into flattened or elongated pores, with nearly parallel walls much nearer together. It is these which I suppose are filled up or sealed with the hydrogenium, first entering as liquid and afterwards solidifying. The liquid hydrogenium would thus permeate the solid metal as mercury permeates metals in amalgamation, and as melted tin or zinc permeates tinned iron plates and 'galvanised' iron. As already explained, these processes of tinning and galvanising are not a mere plating of the surface of the iron by the tin or zinc, but the formation of an alloy which gradually penetrates the iron.

In Vol. XIII. of 'Iron,' page 649, May 24, 1879, is an account of some experiments by Prof. F. C. G. Müller, 'On the Gases enclosed in Iron and Steel.'

The particulars of four experiments, representing a mean of twelve, are stated—1st on Bessemer steel before the addition of the spiegel; 2nd, Bessemer steel from same charge after adding spiegel; 3rd, open-hearth steel; and 4th, pig iron from the cupola. The volume of gas in percentage of the volume of metal was as follows:—1st=60; 2nd=45; 3rd=25; 4th=35. The composition of this gas was:—

	1	2	3	4
Hydrogen	88·8	77·0	67·8	83·3
Nitrogen	10·5	22·9	30·8	14·2
Carbonic oxide . . .	0·7	—	2·2	2·5
	100·0	99·9	100·8	100·0

The experiments were made by casting a 2-inch sample

ingot, cooling it in water, then coating it with wax while still warm. By fixing this to the spindle of a strong drilling machine, a hole was drilled in it under water, the drillings weighed, and the gas collected in the inverted hole. When the first experiment was made showing nearly pure hydrogen, Professor Müller doubted the accuracy of his method, supposing that the hot drillings decomposed some of the water. He therefore repeated the experiments under oil, and found the same result. These experiments assign a much lower proportion to carbonic oxide than is usually represented. I state the results as given, without doubting their accuracy as far as they go, but by the method adopted I believe that they did not go far enough—that only a portion of the gases, and that portion in which the hydrogen greatly predominates, was extracted.

This will appear from the following. Müller's averages were :—

	Steel.	*Pig-iron.*
Hydrogen	77·9	83·3 per cent.
Nitrogen	21·4	14·2 „
Carbonic oxide . . .	1.0	2·5 „

These proportions differ materially from Graham's results, who found much more carbonic oxide and less hydrogen. But Graham operated in a different manner. He heated the iron *in vacuo*, and continued pumping out the gases for some hours. He found that the hydrogen came away the first, and the most readily, followed by increasing quantities of carbonic oxide. Müller merely drilled the metal under water, and collected the gases that were given off under atmospheric pressure plus that of some water. Graham, operating upon wrought iron (horseshoe nails), obtained, after two hours' pumping :—

Hydrogen	35·0 per cent.
Nitrogen	7·0 „
Carbonic oxide	50·3 „
Carbonic acid	7·7 „

After two hours' more of pumping the second portion of gas then extracted contained:—

Hydrogen	21·0 per cent.
Nitrogen	21·0 „
Carbonic oxide	58·0 „
Carbonic acid	none

These great differences suggest the desirability of further experiments. I have little doubt that an extended research into the gases occluded by different qualities of pig-iron, steel, and malleable iron would bring out very interesting results. A sufficient number of samples of each kind to afford a fair average would be required, and all the experiments should be similarly conducted in order to obtain comparable results. When this has been done we shall be able to decide whether occluded gases have any practical influence on the quality of iron and steel, especially if the working qualities of all the samples are practically tested before and after pumping out their occluded gases. The work would be laborious and costly, too much to be expected from an unaided private individual.

One of the direct practical bearings of this subject of occlusion is on the rationale of blisters. All practical readers must share the feelings of the writer, who has been intensely disgusted in watching the passage of a large and costly plate of fine quality through the rolls, and finding that, just at the last finishing squeeze, when all seemed perfect, a big blister deliberately swells up near the middle of the plate, rendering it quite useless for its

intended purpose, only fit for cutting up into small plates of lower value, with the blistered part as mere scrap.

What is the source of these suddenly formed gas bubbles? I first supposed that they are caused by the existence of a little cinder that had found its way between the layers of the piles. This is a common theory. Careful examination of the laminated surfaces within the blister did not confirm this hypothesis, for in no instance could I find any traces of cinder or other visible impurity. The surfaces, on the contrary, were remarkably clean.

There are two circumstances which suggest another explanation. These are that the blister usually rises at the later stages of rolling, and that the skin thus raised is very thin.

From these it appears probable that the gas which does the mischief was there before the blister made its presence evident, but was held down by the resistance of a layer of iron above it, this layer being too thick for it to force upwards. As the rolling proceeds this layer becomes thinner and thinner, its resistance less and less, until at last the expansive energy of the gas is able to overpower it, and then the blister rises.

The fact that the blister generally rises immediately after the part in which it is located has passed under the rolls, further supports this view, as this is the moment when the resistance is removed, and when the part in question is further heated by pressure. When such a blister is pricked there appears to come forth an outpuff of compressed gas.

Here again we have a subject for further experimental research. Such blisters might be pricked under water and the out-bubbling gases collected, measured, and examined. With a knowledge of their composition and

quantity some theory better than mere guesswork might be framed, and possibly, with a knowledge of their causes, the means of prevention might be indicated. The gases producing them may have been originally occluded or simply imprisoned under pressure, and set free in the manner above described.

The blisters on the bars that are subjected to the action of a cementing furnace present another problem suggestive of much speculation. There is less difficulty here in accounting for the existence of gas immediately below the surface of the metal. The bars of iron are coated with a skin of oxide of variable thickness. The first action of the powdered charcoal in which they are embedded and heated must be to reduce the outermost film of this scale to metallic iron. Thus, a thickish coat of scale becomes plated with a skin of iron which almost simultaneously takes up carbon and becomes a skin of steel. The carbonic oxide gas which is formed quite on the surface at the initial stage of reduction escapes directly into the air, but not so when a film of reduced or carburetted metal covers the surface.

The next step of reduction occurs below this, and the gas formed in the course of such reduction must either force its way through or lift it in blisters. It will probably begin by forcing through, and then, as it proceeds a little deeper, lift up some parts of the skin without rupture, the skin being red-hot and viscous.

The appearances presented by the surface of a bar of blister steel confirm these theoretical anticipations. There are blisters and scaly roughness, or disintegration of the skin, instead of the bright smooth surface that should be presented by the conversion of iron into steel, without any such disturbance.

In the course of writing this an experiment is suggested which I am not on the spot to try, but it is so simple and easy to those who are working the old-fashioned cementing furnaces, that I venture to ask for a trial of it. Let one bar, or one side of a bar, be cleaned perfectly from scale, and roughly polished before putting it in the chest of the furnace. When the whole charge is finished, compare the surface of this with those of the other bars as regards the blistering. If this is blistered like the others the explanation above given will not stand, and we must look deeper for an explanation.

The question thus raised will be whether there exists in ordinary iron a sufficient quantity of minute specks of oxide (such as are visibly abundant in burnt iron) to combine with the inflowing carbon, and produce blisters of a deeper character than those above described.

Oxygen anyhow supplied to the inflowing carbon would necessarily produce carbonic oxide, and, if oxygen were one of the occluded gases, the explanation of blistering would be simple enough; but it has not been found among them, and for the reasons already expounded cannot exist as an occluded gas in the midst of heated metallic iron. It would combine chemically and form solid oxide, and does so in 'burnt' iron.

In conclusion, I must apologise for making so many suggestions and appeals for further research while carrying out so few myself. This has especially and necessarily occurred in the present chapter.

A little reflection will show that a lifetime would be insufficient to fairly complete all such experimental investigations, and those additional researches which would of course be suggested in the course of making them. Besides this, most of them demand the use of special appli-

ances not supplied in any ordinary chemical laboratory; appliances only obtainable in great ironworks.

It is only fair to add in reference to this, that our ironmasters generally are remarkably liberal in allowing scientific investigators and inventors to carry on their researches, and test their inventions on a practical scale, at the ironmasters' expense, in the ironmasters' works. The cost of such permission in fuel, iron, and wages, is, in some cases, considerable.

Besides this, we have the Iron and Steel Institute, and ironmasters who themselves devote a large outlay of time, and skill, and money, to such experimental investigations. A notable and noble example is presented by Sir J. Lowthian Bell's researches on the chemistry of the blast furnace, that have supplied me with so much of the material for my chapters on that part of the subject, and for the use of which I desire to express my hearty thanks.

To this British liberality, combined with a robust British contempt for the feeble devices of 'protection,' I attribute much of the British monopoly of the modern progress in iron and steel making, to which allusion is made in the preface and other parts of this volume.

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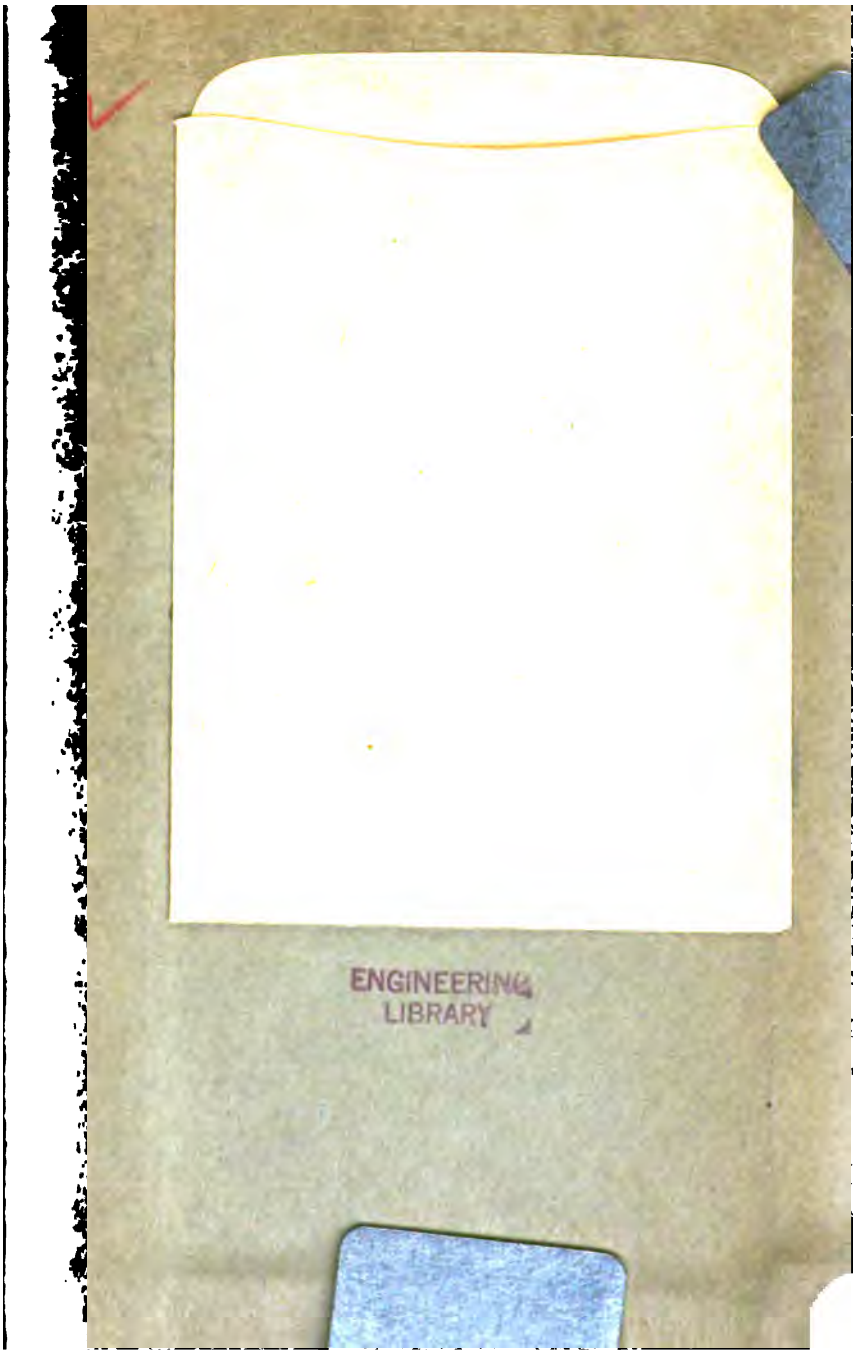
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